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Complexes of Cu(II) with 2,2'-Dipyridyl and Some Cycloalkane-1,1-dicarboxylic Acids*

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The stability constants of ternary complexes containing copper(II), 2,2'-dipyridyl and cyclopropane-1,1-dicarboxylic, cyclobutane-1,1-dicarboxylic and cyclopentane-1,1-dicarboxylic acids, were obtained by potentiometric titrations. The stability order found for these complexes is discussed in terms of ring size influence upon the chelation of the dicarboxylate dianions to the system Cudip. It is suggested that the electronic and geometric characteristics of the strongest ligand drive the coordination of the second one.

Introduction

In a previous paper[1] we discussed the stability of some ternary complexes among copper(II), 2,2'-dipyridyl and a set of substituted malonic acids, in order to achieve informations about the effect of the substituents on the ternary complex stability.

The experimental data obtained in that study were explained in terms of the influence of the alkyl groups on the ability of the dicarboxylate anions to satisfy the coordinating, steric and electronic requirements of the copper(II) ion bound to the 2,2'-dipyridyl. The cycloalkane-1,1-dicarboxylic acids are ligands which give six-membered chelate rings, and can be considered as particular disubstituted malonic acids.

Hence, to verify the validity of the previous hypotheses on the framework effect of these ligands on the stability of the ternary complexes of Cu(II) with 2,2'-dipyridyl, potentiometric studies have been carried out on these systems, and in particular the complexes of Cu(II) with 2,2'-dipyridyl (dip) and cyclopropane-1,1-dicarboxylic (CPRD), cyclobutane-1,1-dicarboxylic (CBUD) and cyclopentane-1,1-dicarboxylic (CPED) acids, were considered.

Potentiometric studies of the complexes with these ligands and transition metals have been reported[2–4]; for all the ions, the stability of the mono-complexes was found to decrease with increasing the size of the ligand ring. The formation of mixed complexes of Cu(II) with cyclobutane-1,1-dicarboxylic acid and other O,O-ligands have been already studies by e.s.r.[5]

Experimental

Reagents

Twice-distilled water was used in the preparation of all the solutions. Sodium perchlorate solutions were prepared from the recrystallized material (C. Erba RP).

Perchloric acid solutions were obtained by diluting the concentrated one (C. Erba 70% RP-ACS) and were standardized with THAM (tris-hydroxymethyl-aminomethane).

Carbonate-free sodium hydroxide solutions were prepared by diluting a saturated solution made up from pellets (C. Erba RP) and twice-distilled water which was flushed with nitrogen and stored free from CO_2 in an automatic burette. The solutions were standardized by titration with both potassium hydrogen phtalate (Merck 'zur analize' dried at 120° C for 2 hr) and perchloric acid solutions.

Copper(II) perchlorate was obtained by dissolution of the basic carbonate in perchloric acid. Stock solutions of $Cu(ClO_4)_2$ were standardized by titration with ethylenediaminetetra-acetic acid (C. Erba RP disodium salt) by using the purification and the indicator recommended by Flashka[6].

Cyclobutane-1,1-dicarboxylic acid (Fluka) was firstly purified with boiling benzene and then recrystallized from 1:1 ether–benzene containing *ca.* 5% of light petroleum.

Cyclopropane-1,1-dicarboxylic and cyclopentane-1,1-dicarboxylic acids were prepared by basic hydrolysis of diethyl esters (Fluka), and were recrystallized in the same way used for cyclopropane-1,1-dicarboxylic acid[7].

After drying in a vacuum desiccator over $CaCl_2$, the acids were dissolved in twice-distilled water and titrated with standard CO_2-free NaOH, under nitrogen atmosphere, to establish their purity. The melting points[8]

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TABLE I. Melting Points and Purity of Cycloalkane-1,1-dicarboxylic Acids.

Acid	Found °C	Lit. °C	Purity %
CPRD	135	136[a]	99.5 ± 0.3
CBUD	162	159[a]	99.8 ± 0.1
CPED	196	190[a]	99.6 ± 0.2

[a] From reference 8.

and the purity (%) of the acids are listed in Table I. 2,2′-dipyridyl (C. Erba RPE) was recrystallized from water–ethanol mixture.

Apparatus

The e.m.f. during the titrations was measured with an Amel potentiometer type 332. The electrodes used for determination of hydrogen ion concentration were an Ingold (201 NS) glass electrode and an Ingold (303 NS) saturated calomel electrode (to avoid precipitation of potassium perchlorate, the calomel electrode contained NaCl in place of KCl). The temperature of the titration vessel was maintained at 25 ± 0.1 °C by pumping thermostated water through the mantle of the vessel by means of a Colora (NB/DS 997) thermostat. The titrant was added by an Amel 10 ml motorized type 233 burette. Magnetic stirring was employed.

Procedure

The formation constants of Cudip with the cycloalkane-1,1-dicarboxylic acids were determined potentiometrically. The free concentration of the dicarboxylic acid (L) was changing systematically by titration of 100 ml solution containing $CU(ClO_4)_2$, 2,2′-dipyridyl and H_2L (1:1:1; 1:1:2; 1:1:3; $Cu(ClO_4)_2$ 6–9 × $10^{-4} M$) with known volumes of standard CO_2-free NaOH. After every addition the e.m.f. was measured waiting for 5 min, when stable and reproducible potentials were reached. The reproducibility was usually within 0.005 pH unity. CO_2 was expelled from the cell solutions by nitrogen which was previously passed through a 0.1 *M* $NaClO_4$ solution. At least 6 titrations were performed for each system. The electrode system was standardized by titrating $HClO_4$ solutions of known concentration with standard NaOH solutions. E° was checked before and after each titration: the observed difference did not exceed 0.25 mV. The change of the ionic strength (I = 0.1 *M* (H,Na) ClO_4) during the titration was less than 5%.

Calculations

The formation constants of the ternary complexes were refined by the program SCOGS[9] on a CDC 6600 computer. This program refines values by an iterative least squares method based on minimizing the sum of squares of differences between computed and experimental titres:

$$U = \Sigma\,(v_{i,\mathrm{exp.}} - v_{i,\mathrm{calc.}})^2$$

The estimated standard deviation (σ_β) in the equilibrium constant value provides a measure of precision, and the standard deviation in titre (σ_v), which in our case was less than 0.013 in all the systems studied, is a measure of the ability of the refined values to reproduce the experimental data. Initial estimates of equilibrium constants were required by the program SCOGS before refinement could begin. The estimates of β^{Cu}_{CudipL} were made from the constants K^{Cu}_{Cudip} and K^{Cu}_{CuL}, according to the following expression:

$$\log\beta^{Cu}_{CudipL} = \log K^{Cu}_{Cudip} + \log K^{Cu}_{CuL}$$

Although the differences between these estimates and the real values of the formation constants of the ternary complexes with CPRD and CBUD are greater than one logarithmic unity, convergence was reached in 5–7 cycles.

Results and Discussion

The values of β^{Cu}_{CudipL} relative to the following equilibrium:

$$\mathrm{Cu} + \mathrm{dip} + \mathrm{L} \rightleftharpoons \mathrm{CudipL}^{*},$$

the literature ones relative to the protonation of the acids, and the formation constants of the mono- and bis-complexes with copper(II)[2,4] are reported in

TABLE II. Logarithms of Acidity Constants of Cycloalkane-1,1-dicarboxylic Acids and 2,2′-dipyridyl, Logarithms of Stability Constants of Their Binary and Ternary Complexes with Copper(II) at I = 0.1 *M* (H, Na)ClO_4 and 25 ± 0.1 °C (the figures in parentheses are the standard deviations in the last decimal figure).

Ligand	$\log K_{HL}{}^{H}$	$\log K_{H_2L}{}^{HL}$	$\log K_{CuL}{}^{Cu}$	$\log K_{CuL_2}{}^{CuL}$	$\log\beta_{CuL_2}{}^{Cu}$	$\log\beta_{CudipL}{}^{Cu}$
CPRD	7.22[a]	1.68[a]	5.99[a]	3.62[a]	9.61[a]	15.52(4)
CBUD	5.55[b]	3.01[b]	5.02[b]	3.47[b]	8.49[b]	14.28(5)
CPED	5.80[a]	3.09[a]	4.89[a]	2.80[a]	7.69[a]	13.30(2)
dip	4.47[c]	–	8.15[c]	5.50[c]	13.65[c]	–

[a] From reference 4. [b] From reference 2. [c] From reference 10.

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* Charges were omitted for the sake of simplicity.

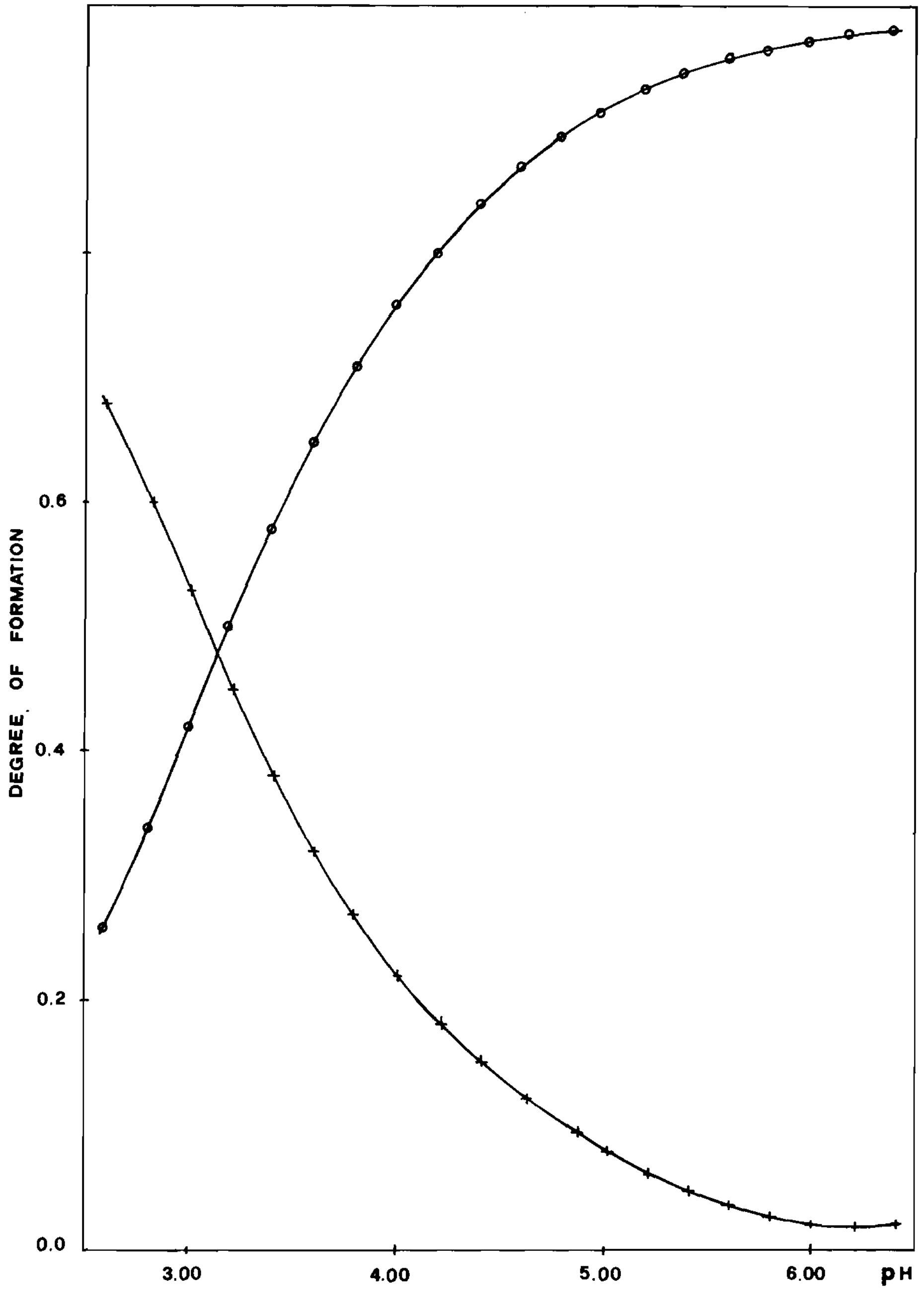

Figure 1. Variation with pH of the concentrations (given as the degree of formation) of the species present in aqueous solutions of copper(II), 2,2′-dipyridyl and cyclopropane-1,1-dicarboxylic acid (each $7.5 \times 10^{-4} M$).

+ Cudip

O CudipCPRD

Table II. Distribution diagrams of the species present in solution for all the systems considered in this study are reported in Figures 1, 2 and 3.

As one can see from data reported in Table II the overall stability constants of the ternary complexes have very different values; a similar pattern is shown by the bis-complexes of cycloalkane acids with a lowered difference. Moreover, there is no simple relation between the basic properties of these acids and the stability of their ternary complexes.

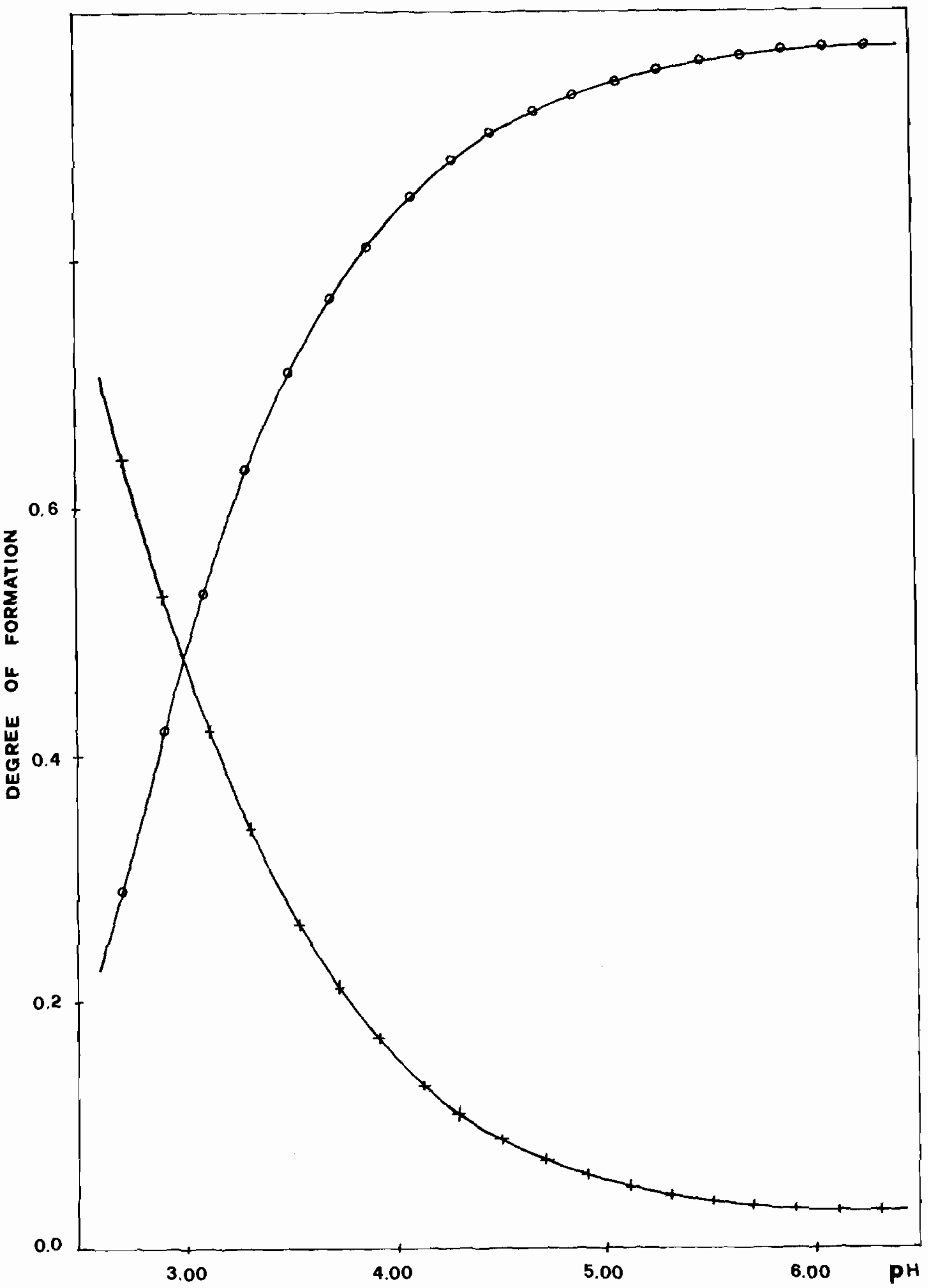

Figure 2. Variation with pH of the concentrations (given as the degree of formation) of the species present in aqueous solutions of copper(II), 2,2'-dipyridyl and cyclobutane-1,1-dicarboxylic acid (each $7.5 \times 10^{-4} M$).
+ Cudip
O CudipCBUD

As we found in the case of the complexes among copper(II), 2,2'dipyridyl and substituted malonic acids[1], in these systems the copper(II) exhausts its coordinating capacities in the tetracoordination level; in fact, we only found ternary species alone in the ratio 1 : 1 : 1. The formation of these complexes seems to be favoured by the neutralization of the metal charges and by the presence of π bonding between the metal and both ligands[11, 12].

Since the former of these factors is always present

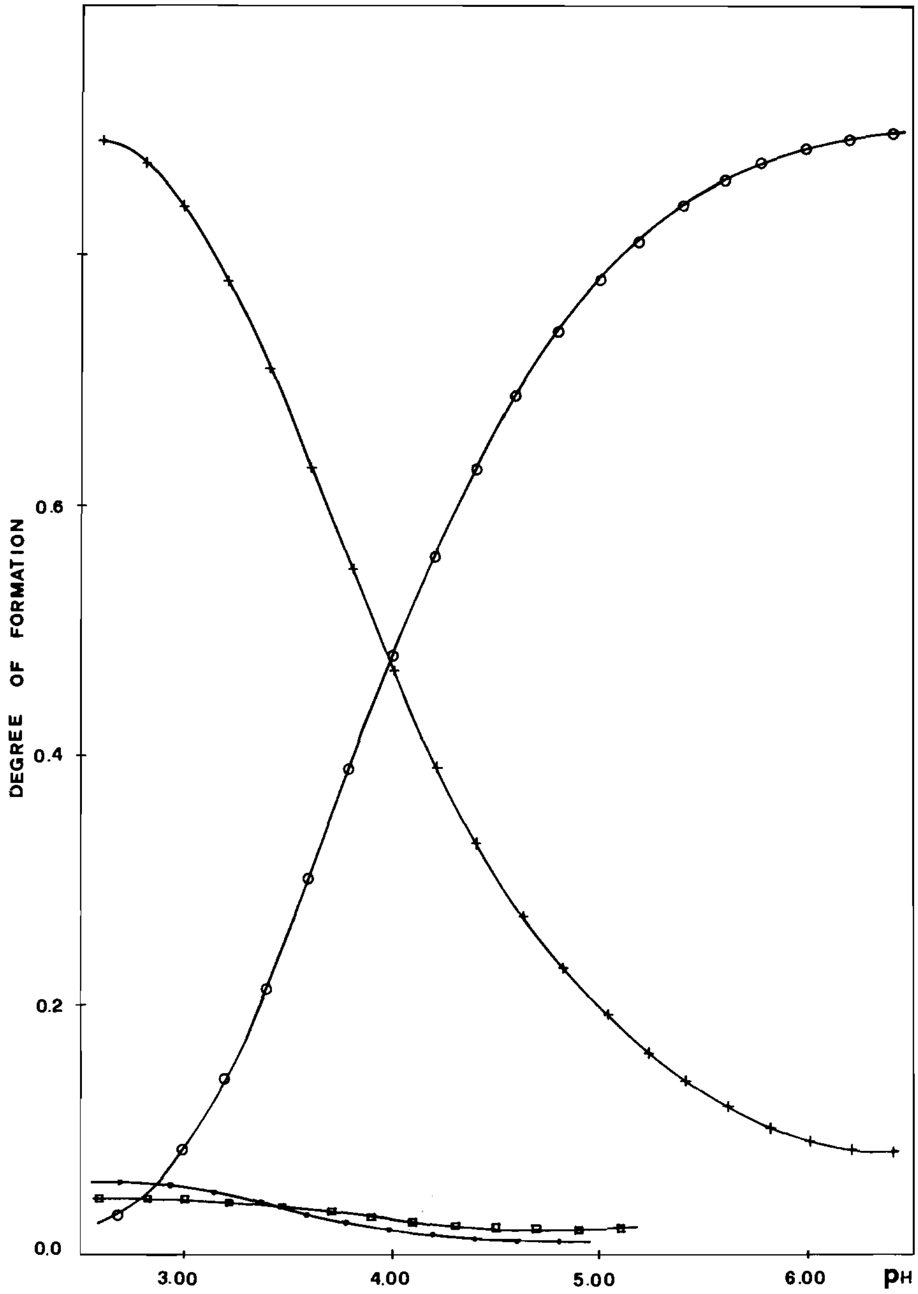

Figure 3. Variation with pH of the concentrations (given as the degree of formation) of the species present in aqueous solutions of copper(II), 2,2′-dipyridyl and cyclopentane-1,1-dicarboxylic acid (each $7.5 \times 10^{-4} M$).

+ Cudip . Cu

○ CudipCPED □ $Cudip_2$

in the systems under investigation, the great difference can be explained in terms of the substrate effect on the electronic and geometric characteristics of these complexes. This effect cannot be only explained considering the internal strain of the alicyclic ring, as it was done for binary complexes[4]; this fact is clearly shown from literature data relative to the ring properties. In particular, all the models concerning the electronic distribution in the cyclopropyl ring imply regions of high electron density outside the ring; moreover, the

Walsh model predicts a relatively deficient electron density in the center of the ring[12]. Hence, electron donating or withdrawing substituents have the possibility of conjugating with the electron affluent edge or electron deficient center of the ring. This pecularity of the three-membered alicyclic ring allows its ternary complex to have a great stability because it favours the π-donor properties of the carboxylate groups, making the bond between the copper(II) and the 2,2′-dipyridyl stronger ("cooperative effects" have been also discussed for similar systems[14]), and giving no interference in the respective coplanarity of both carboxylate groups, a condition requested by the coordination of the copper(II) to 2,2′-dipyridyl.

About the four-membered alicyclic ring, there is a great number of recent works regarding the equilibrium structures of cyclobutane and its derivatives[5,6]; in particular, the results reported for the cyclobutane-1,1-dicarboxylic acid[7] allow to affirm that the skeleton of the cyclobutane in this compound is approximately flat. The difference found for the β^{Cu}_{CudipL} values between the systems containing CBUD and CPRD, can be explained considering the dramatic change in conjugating properties on going from cyclopropane to cyclobutane.

Even if the difference in the pK values of CBUD and CPED is negligible, the complexes with CPED have lower stability constant values than those of the complexes with CBUD. Since the cyclopentane ring (certainly lacking electronic effects) adopts a puckered conformation[8] and its β^{Cu}_{CudipL} value is very similar to those found for the systems CudipX–MAL (where X–MAL is the abbreviation of a generic mono-substituted malonic acid), it is probable that nonbonded interactions[9] are responsible for such a behaviour in the relative stability between CudipCPED and Cudip CBUD. It has been observed that the existence of nonbonded atoms often seems to exert a great influence in governing the geometry. Hence, it is probable that the increase in size (with consequent possibilities in adopting puckered conformations) going from CBUD to CPED, influences indirectly the respective coplanarity of the carboxylic groups, making the coordination to the system Cudip more difficult.

The values found for ΔlogK and $\log K_r$[20] (parameters generally used for indicating the stabilization of the ternary complex with respect to the binary one, the range of validity of which, in our opinion, has not yet been verified) defined according to the following expressions:

$$\mathrm{Cudip} + \mathrm{CuL} \rightleftharpoons \mathrm{CudipL} + \mathrm{Cu}$$

$$\Delta \log K = \log\beta^{Cu}_{CudipL} - (\log K^{Cu}_{Cudip} + \log K^{Cu}_{CuL})$$

$$\mathrm{Cudip_2} + \mathrm{CuL_2} \rightleftharpoons 2\ \mathrm{CudipL}$$

$$\log K_r = 2\log\beta^{Cu}_{CudipL} - (\log\beta^{Cu}_{Cudip_2} + \log\beta^{Cu}_{CuL_2})$$

are reported in Table III.

TABLE III. Stabilization Parameters ΔlogK and $\log K_r$ for Ternary Complexes of Copper(II), 2,2′-dipyridyl and Cycloalkane-1,1-dicaroxylic Acids, and Other Similar Systems at I = (H, Na)ClO$_4$ 0.1 *M* and 25 ± 0.1° C.

System	ΔlogK	$\log K_r$	Ref.
CudipCPRD	1.38	7.78	this work
CudipCBUD	1.11	6.42	this work
CudipCPED	0.26	5.26	this work
CudipOx[a]	0.70	4.90	21
CudipMAL[a]	0.25	5.65	1
CudipPyr[a]	0.43	6.15	22
CudipSal[a]	0.27	5.70	22

[a] The symbols Ox, MAL, Pyr and Sal are used for oxalic acid, malonic acid, pyrocathechol and salicylic acid respectively.

These values support the considerations previously made. One can see from the Table III that the systems with alicyclic three- and four-membered rings give values of these parameters particularly higher than those obtained for similar systems containing copper(II), 2,2′-dipyridyl and O,O-donor ligands already known in literature; the complex CudipCPRD shows the highest values for ΔlogK and $\log K_r$ found till now.

On the ground of the previous discussion about the stability of these systems, there is evident the strong influence of the conjugating characteristics of the substrate of dicarboxylate groups and the driving forces of 2,2′-dipyridyl on the formation of these mixed complexes. Both these factors seem to play an important role, since the 2,2′-dipyridyl in chelating to the copper(II) ion prearranges the metal in the best way to accept the dicarboxylate anion. The order of β^{Cu}_{CudipL} values found for these systems can be reasonably ascribed not only to the σ-donor properties of O-donor ligands[23], but also to the π-donor characteristics of the oxygen atoms which are strongly influenced by the substrate of the dicarboxylate anions.

To clarify better' the influences of the electronic characteristics of the ligands on the properties of the ternary complexes here reported, spectroscopic studies are in progress.

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