Inorganica Chimica Acta, 18 (1976) 155–158

Complexes of Cu^{2+} with 2,2′-Dipyridyl and Cyclohexane-1,1-dicarboxylic Acid

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Received September 20, 1975

Formation and stability of the mixed complexes of Cu^{2+}–2,2′-dipyridyl with cyclohexane-1,1-dicarboxylic acid have been investigated by means of potentiometric measurements of hydrogen ion concentration, at 25° C and in a medium 0.1 M (Na,H)ClO_4. Complexes as CuDipL and $CuDipL_2$ have been considered. Hamilton test applied to this system cannot confirm or exclude the hypothesis of formation of the complex $CuDipL_2$, whose real existence is considered unlikely on the ground of enthalpic and entropic considerations. Relating the stability of CuDipL to that of other mixed complexes of CuDip with some 1,1-dicarboxylic acids previously studied one can point out the influence of the alicyclic ring rigidity on the stability of the mixed complexes.

Introduction

Previously[1] we studied the stability of the mixed complexes of Cu^{2+}–2,2′-dipyridyl with some alicyclic-1,1-dicarboxylic acids (three-, four- and five-membered rings). We found it very interesting to study the influence of the alicyclic ring size on the stability of such mixed complexes. This influence can be evidenced by different factors, such as the steric and electronic characteristics of the rings.

In this work we investigate the formation and the stability of the mixed complexes of Cu^{2+} with 2,2′-dipyridyl (Dip) and cyclohexane-1,1-dicarboxylic acid (L). To determine formation constants, we used the pH-metric method, which is very efficient for this type of systems.

Experimental

Reagents

Cyclohexane-1,1-dicarboxylic acid was synthesized by reaction between diethyl esther of the malonic acid and 1,5-dibromopentane according to Vogel's procedure[2]. The melting point of the product was 183° C (Vogel, 179.5° C); its purity was also tested by means of titrations with standard solutions of NaOH and a value of 99.85 ± 0.08% (mean of 6 determinations) was found. Sodium hydroxide, copper(II) perchlorate and perchloric acid solutions were obtained as previously described[1,3].

Apparatus

Potentiometric titrations were performed with two different equipments, the characteristics of which are reported in Table I. Other details were reported previously[1,3].

Determination of Equilibrium Constants

The protonation constants of 2,2′-dipyridyl and cyclohexane-1,1-dicarboxylic acid, and the formation constants of the mixed species were determined by pH-metric method. The initial conditions relative to the titrations are listed in Table II. The measurement and calibration solutions were at ionic strength 0.1 *M* (Na,H)ClO_4; this value changed during the titrations within 5%. All the measurements were performed at 25 ± 0.1° C. The formation constants of the species CuDip and $CuDip_2$ were recalculated from Irving and Mellor data[4]. The formation constants of the species CuL and CuL_2 were taken from the work of Ostacoli and co-workers[5].

TABLE I. Characteristics of the Equipments Used for the Potentiometric Measurements.

Equipment	pH-meter	Resolution (mV)	Accuracy (mV)	Burette	Resolution (ml)	Accuracy (ml)	Electrodes Glass–Calomel
A	Radiometer PHM 52 b	0.1	0.2	Radiometer ABU 12 b	0.001	0.003	Radiometer G2025C–K4025
B	Amel 332	0.1	0.15	Amel 233	0.01	0.015	Ingold 201NS–303NS

TABLE II. Protonation and Complex Formation Determination.

Solution	Initial Concentrations[a] ($M \times 10^4$)			pH Range
	C_{Cu}	C_L	C_{Dip}	
1	5.0	5.0	5.0	3.2–5.2
2	5.0	10.0	5.0	3.5–6.1
3	7.5	30.0	7.5	3.3–6.1
4	–	77.5	–	2.7–6.0
5	–	90.0	–	2.7–6.1
6[b]	–	–	75.0	3.5–4.9
7[b]	–	–	40.0	3.6–5.0

[a] Rounded off to the first decimal place. [b] Initial concentration of $HClO_4$: $1.2C_{Dip}$.

Calculations

We used the computer program SCOGSB, derived from the program SCOGS[6], to calculate the formation constants. This program minimizes the error squares sum $U = \Sigma(V_o-V_c)^2$, where V is the titre and the indexes o and c indicate respectively the observed and calculated quantities. We made the following changes to the original program: a) the mass balance equations have been reduced to three (one metal and two ligands); b) the free concentrations of the metal and ligands are memorized in order to be used for the successive cycle[7]; c) the numerical differentiation is made by interpolation on five points (three in the original program); d) the inverse of the coefficient matrix A, A^{-1}, is obtained from the eigenvalues and eigenvectors[8], to overcome the difficulties of near singularities of matrix A; e) one can elaborate titration data in which the titrant is a ligand (*e.g.* a weak acid totally or partially salified) as well as a strong base or a strong acid; some parts of the program were completely modified in order to speed up the calculations. These modifications make the program more flexible and rigorous, and allow us to spare calculation time (*ca.* 60%). A subroutine, TESTFIT, which analyzes statistically the residuals, was added to the program. In this subroutine the residuals are subdivided in classes and for every class the theoretical frequency is calculated from the equation of the normal distribution, from which it is possible to calculate: $\chi^2 = \Sigma(O_i-T_i)^2/T_i$, where O_i is the observed frequency of the i-th class and T_i is the corresponding theoretical frequency. Then the integral $P(\chi^2,\nu)$ is calculated from the equation of the chi-square distribution[9] (ν is the number of degrees of freedom). The skewness and kurtosis coefficient, $\mu_j = \Sigma r_i^j/N^j$ (j = 3, 4), are calculated, and allow us to know how much the distribution of the residuals (r_i) shifts from normal distribution (the theoretical values of the skewness and kurtosis coefficient are respectively 0 and 3, and the conditions for a distribution to be closed to a normal one are: $-2<\mu_3<+2$; $\mu_4\sim 3$ and $\mu_4>\mu_3^2+1$). Finally, the R Hamilton factor[10], $R = (\Sigma r_i^2/\Sigma V_i^2)^{1/2}$, is calculated. In the case of different hypotheses on the types of species that are present in a certain system, we shall obtain different R values; in such a case, the Hamilton test[10] can be applied to this type of problem[11].

To recalculate the formation constants of the species CuDip and $CuDip_2$, from the data of Irving and Mellor[4], and for the calculation of protonation constants of cyclohexane-1,1-dicarboxylic acid, the program PMGZ[12] was employed. This program minimizes the error squares sum $U = \Sigma(\bar{n}_o-\bar{n}_c)^2$, where $\bar{n}$ is the average number of ligands bound per central atom.

All the calculations were carried out by means of a CDC 6600 computer.

Results and Discussion

The measurements performed by means of the equipments A and B were at first considered separately and then together; in all cases we obtained comparable results.

The species HDip, HL,H_2L, CuL, CuL_2, CuDip, $CuDip_2$ and CuDipL were taken into account, and the relative equilibria are listed in Table III. The distribution diagram of the system Cu^{2+}–2,2′-dipyridyl–cyclohexane-1,1-dicarboxylic acid is reported in Figure 1.

We also examined the possibility of formation of the complex $CuDipL_2$. If we consider only the formation

TABLE III. Equilibria in Solutions Containing Cu^{2+}, 2,2′-Dipyridyl and Cyclohexane-1,1-dicarboxylic Acid, at 25° C and Ionic Strength 0.1M (Na,H)ClO_4.

Equilibrium	Formation Constant ± Standard Deviation
Dip + H = HDip	4.461 ± 0.005
L + H = HL	5.695 ± 0.005
HL + H = H_2L	3.290 ± 0.005
L + 2H = H_2L	8.985 ± 0.005
Cu + L = CuL	4.62 ± 0.02[a]
CuL + L = CuL_2	2.62 ± 0.02[a]
Cu + 2L = CuL_2	7.24 ± 0.03[a]
Cu + Dip = CuDip	8.14 ± 0.03[b]
CuDip + Dip = $CuDip_2$	5.50 ± 0.04[b]
Cu + 2Dip = $CuDip_2$	13.64 ± 0.05[b]
Cu + Dip + L = CuDipL	13.048 ± 0.005
CuDip + L = CuDipL	4.91 ± 0.03
CuL + Dip = CuDipL	8.43 ± 0.02
$CuDip_2$ + CuL_2 = 2CuDipL	5.22 ± 0.06
CuDip + CuL = CuDipL + Cu	0.29 ± 0.04

[a] Ref. 5. [b] Values recalculated with the data taken from Ref. 4. Ionic strength 0.1M KCl.

TABLE IV. Formation Constants of Ternary Complexes of Copper(II) with 2,2′-Dipyridyl and Cyclohexane-1,1-dicarboxylic Acid, Using Different Hypotheses.

Formation Constants ± Standard Deviation		$P(\chi^2, \nu)$	μ_3	μ_4	R
CuDipL	$CuDipL_2$				
13.044 ± 0.005	15.0 ± 0.1	0.98	0.27	2.63	0.0029
13.048 ± 0.005	–	0.99	0.13	2.97	0.0030

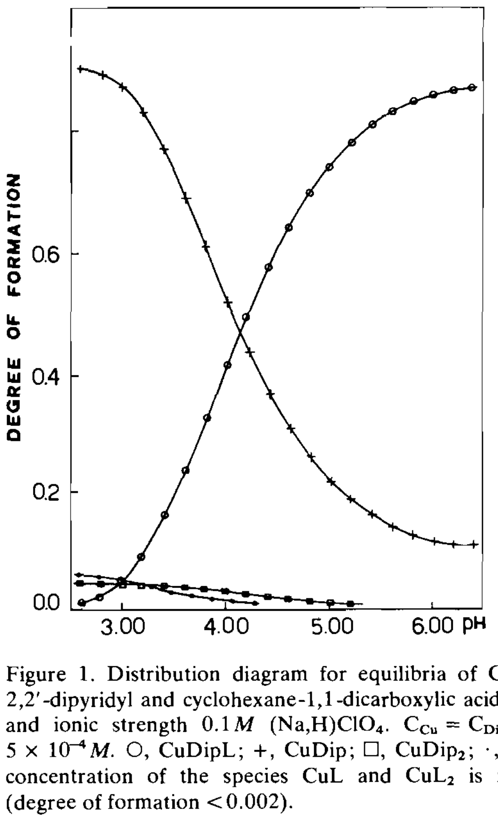

Figure 1. Distribution diagram for equilibria of Cu^{2+} with 2,2′-dipyridyl and cyclohexane-1,1-dicarboxylic acid at 25° C and ionic strength 0.1*M* $(Na,H)ClO_4$. $C_{Cu} = C_{Dip} = C_L = 5 \times 10^{-4}$*M*. ○, CuDipL; +, CuDip; □, $CuDip_2$; ·, Cu. The concentration of the species CuL and CuL_2 is negligible (degree of formation <0.002).

TABLE V. $\log\beta_{11}$, $\Delta\log K$ and $\log K_r$ Values[a] of Ternary Complexes of Cu^{2+} with 2,2′-Dipyridyl and Cycloalkane-1,1-dicarboxylic Acids, at 25° C and Ionic Strength 0.1 *M* $(Na, H)ClO_4$.

Dicarboxylic Acid	$\log\beta_{11}$	$\Delta\log K$	$\log K_r$
Cyclopropane-1,1-	15.52	1.38	7.78[b]
Cyclobutane-1,1-	14.28	1.11	6.42[b]
Cyclopentane-1,1-	13.30	0.26	5.26[b]
Cyclohexane-1,1-	13.05	0.29	5.22

[a] $\beta_{11} = [CuDipL]/[Cu][Dip][L]$; $\Delta\log K = \log\beta_{11} - (\log K^{Cu}_{CuDip} + \log K^{Cu}_{CuL})$; $\log K_r = 2\log\beta_{11} - (\log\beta^{Cu}_{CuDip_2} + \log\beta^{Cu}_{CuL_2})$.

[b] Ref. 1.

of the mixed species CuDipL, we obtain an R_1 value equal to 0.0030 (see Table IV), whereas if we introduce the mixed species $CuDipL_2$, we obtain an R_o value equal to 0.0029. The ratio R_1/R_o is not even significant at 2.5% significance level (for a number of degrees of freedom equal to 90).

Then we can choose one of two hypotheses only on the ground of chemical considerations. We consider the first hypothesis reliable because several factors make the real existence of the species $CuDipL_2$ unlikely: a) the neutral mixed complex is entropically more stable than the ionic one; b) the presence of π-bond among the cupric ion, 2,2′-dipyridyl[13], and the dicarboxylic ligand, as was hypothesized for the complex Cu–oxalic acid[14], stabilizes the tetracoordinated species[15]; c) even molecules with high 'N.D.' value[16] as DMSO do not modify the coordination number, as was verified for this system and similar others[17].

To enhance the influence of the alicyclic ring size on the stability and the 'stabilization' of the mixed complexes Cu^{2+}–2,2′-dipyridyl–alicyclic-1,1-dicarboxylic acids, we report in Table V the values of β_{11}, $\Delta\log K$ and $\log K_r$ of the systems previously reported[1] and of the one studied in this work. For the system we investigated, the experimental results are very close to the ones relative to CuDipCPED and then clearly different from those relative to CuDipCPRD and CuDipCBUD.

Similarly to CPED, the cyclohexane-1,1-dicarboxylic acid ring has not a particular electronic property, as it is known to have a chair conformation. Taking into account this characteristic conformation, we can surmise that probable non-bonded interactions oppose to the coplanarity of the two carboxylic groups. Consequently, the ligand does not meet the coordination requirements of Cu^{2+}–2,2′-dipyridyl and shows a behaviour similar to that of the monosubstituted malonic acids, for which such a hypothesis allowed to explain the results[18] obtained for such systems.

Acknowledgement

We thank C.N.R. (Rome) for financial support to this work.

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