*Inorganica Chimica Acta*, 27 (1978) 31–35

# Potentiometric Investigation of Simple and Mixed Complexes of Cupric Ion in Aqueous Solution

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Received June 14, 1977

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*Simple and mixed complexes of copper(II) with 2,2'-dipyridyl and oxydiacetic or thiodiacetic acid have been investigated at 25 °C in 0.1* M *($NaClO_4$) by potentiometric measurements. Stability constants for the systems CuL, $CuL_2$, CuHL, Cu(dip)L, Cu(dip)HL (where L is oxydiacetic or thiodiacetic acid and dip is 2,2'-dipyridyl) have been determined.*

*Some considerations about the stability of these complexes are reported.*

## Introduction

In the literature one finds few reports on mixed complexes of cupric ion with ligands which together have more than four donor atoms grouped around the metal ion, in respect to the number of works on the formation and stability of the mixed complexes of this ion concerning bidentate ligands [1, 2]. This lack of information on the effect of the coordination level of cupric ion ternary systems is due to the fact that i) the mixed complexes of copper(II) with bidentate ligands are generally more stable than the parent complexes; ii) increasing the number of donor sites makes it more difficult to determine the coordination level by evaluating only the stability constants.

Since Sarkar *et al.* [3–5] found that the exchangeable portion of copper(II) in blood plasma occurs mainly as a result of the mixed complex formation, these systems are being more intensively investigated as they can be taken as models, provided that there is a prevalent number of polydentate ligands in biological fluids. Recently we have investigated both the mixed complexes of cupric ion with 2,2',2''-terpyridyl and dicarboxylic acids, and those with 2,2'-dipyridyl and dipicolinic or iminodiacetic acid [6]; these ligands have a total of more than four donor atoms. Every system previously investigated by us had the same number of donor atoms, *i.e.* three nitrogens and two oxygens. We found it interesting to investigate the complexes of copper(II) with 2,2'-dipyridyl (dip) and oxydiacetic (ODA) or thiodiacetic (TDA) acid, which have the same number of donor atoms as the above-mentioned systems but a different environment, in order to check whether or not the heteroatom is bonded.

The measurements relative to the determination of the formation constants of both ternary and parent complexes as well as of the protonation constants have been carried out potentiometrically at ionic strength I = 0.1 *M* ($NaClO_4$) and at t = 25 °C.

## Experimental

### *Reagents*

The 2,2'-dipyridyl (Erba R.P.) was recrystallized from a water–ethanol mixture; the acids (Fluka) were recrystallized as described in the literature. The purity was checked by potentiometric titrations with standard NaOH solutions and was assumed as good when it was over 99%. NaOH solutions were made up by diluting NaOH concentrated solutions, previously cooled and filtered, in order to eliminate the sodium carbonate; they were standardized with potassium hydrogen phthalate (Merck). The perchloric acid diluted solutions were prepared as described by Grenthe *et al.* [7]. The copper perchlorate was prepared from basic carbonate and perchloric acid; then it was recrystallized several times and dried under vacuum. The $Cu(ClO_4)_2$ solutions were standardized both by titrations with EDTA (murexide as indicator) and by electrodeposition.

All the solutions were prepared with twice-distilled water, carbon dioxide free, and kept at ionic strength 0.1 *M* by adding $NaClO_4$.

### *Apparatus*

The potentiometric measurements were performed using an Orion 801 A potentiometer equipped with an EIL glass electrode and with a double junction saturated calomel electrode. The titrations were carried out in a 100 ml cell which was kept at 25 ± 0.5 °C by means of a Colora NB/DS 997 thermostatic bath. The solution vessel was also maintained in an oxygen and carbon dioxide free atmosphere of purified nitrogen, previously bubbled through 0.1 *M*

TABLE I. Proton Association Constants of Oxydiacetic, Thiodiacetic, Selenodiacetic and Tellurodiacetic Acids.

| Medium (*M*) | Temp (°C) | $\log K_{HL}$ | $\log K^{HL}_{H_2L}$ | Ref. |
|---|---|---|---|---|
| | | L = oxydiacetic acid | | |
| 0.1 KCl | 30 | 4.03 | 2.90 | 14 |
| 0.1 | 25 | 3.92 | 2.77 | 15 |
| 0.1 | 20 | 4.11 | 3.06 | 16 |
| 0.1 ($NaClO_4$) | 25 | 3.89 ± 0.01 | 2.83 ± 0.01 | [a] |
| | | L = thiodiacetic acid | | |
| 0.1 KCl | 30 | 4.29 | 3.26 | 14 |
| 0.1 | 25 | 4.13 | 3.15 | 15 |
| 0.1 | 20 | 4.35 | 3.30 | 16 |
| 0.1 $NaClO_4$ | 25 | 4.14 | 3.13 | 17 |
| 0.1 ($NaClO_4$) | 25 | 4.09 ± 0.01 | 3.13 ± 0.02 | [a] |
| | | L = selenodiacetic acid | | |
| 0.1 ($KNO_3$) | 25 | 4.345 | 3.266 | 12 |
| | | L = tellurodiacetic acid | | |
| | | 4.77 | 3.26 | 13 |

[a] This work.

TABLE II. Formation Constants of Copper(II) Complexes with Oxydiacetic, Thiodiacetic and Selenodiacetic Acids.

| Medium (*M*) | Temp (°C) | $\log K^{Cu}_{CuL}$ | $\log K^{CuL}_{CuL_2}$ | $\log K_{CuHL}$ [b] | Ref. |
|---|---|---|---|---|---|
| | | L = oxydiacetic acid | | | |
| 0.1 KCl | 30 | 3.9 | – | – | 14 |
| 0.1 | 25 | 3.9 | – | – | 15 |
| 0.1 | 20 | 3.70 | – | 2.67 | 16 |
| 0.1 ($NaClO_4$) | 25 | 4.18 ± 0.01 | 1.7 ± 0.1 | 2.92 ± 0.05 | [a] |
| | | L = thiodiacetic acid | | | |
| 0.1 KCl | 30 | 4.5 | 2.8 | – | 14 |
| 0.1 | 25 | 4.3 | – | – | 15 |
| 1.0 ($ClO_4^-$) | 20 | 4.18 | 2.9 | – | 18 |
| 0.1 | 20 | 4.57 | – | 3.18 | 16 |
| 0.1 $NaClO_4$ | 25 | 4.59 | 2.87 | 2.63 | 17 |
| 0.1 ($NaClO_4$) | 25 | 4.45 ± 0.01 | 2.60 ± 0.04 | 2.60 ± 0.05 | [a] |
| | | L = selenodiacetic acid | | | |
| 0.1 ($KNO_3$) | 25 | 3.55 | – | 2.50 | (12) |

[a] This work. [b] The constant $K_{CuHL}$ refers to the reaction $Cu + HL \rightleftharpoons CuHL$.

$NaClO_4$ solution. The electrodes were calibrated by titrating perchloric acid with sodium hydroxide. The titrant was added from a piston Methrom Dosimat E 415 burette or a motorized Radiometer ABU12 burette. Magnetic stirring was employed.

### *Procedure*

The formation constants relative to the copper(II) with oxy- and thiodiacetic acid complexes were determined by titrating 70–100 ml of ligand and copper(II) perchlorate solutions (in which $[Cu]_T$ = 2–5 m*M* and $[L]_T/[Cu]_T$ = 0.5:1, 1:1, 2:1, 3:1, 4:1, 5:1) with NaOH 0.1 or 0.5 *M* standard solutions. For each system at least ten titrations were carried out. The formation constants relative to the copper(II)–2,2′-dipyridyl system were reported in a previous paper [8]. The formation constants of the ternary systems were determined by titrating 100 ml of solution containing 2,2′-dipyridyl, copper(II) perchlorate and oxy- or thiodiacetic acid (in which $[Cu]_T$ = $[dip]_T$ = 0.8–0.9 m*M* and $[L]_T$ = 1–6 m*M*) with 0.1, 0.2 or 0.5 *M* NaOH standard solutions. For each system at least six titrations were performed.

TABLE III. Formation Constants of 1:1 Complexes of Some Metal Ions with Oxydiacetic and Thiodiacetic Acids.

| M | $\log K^{Cu}_{CuL}$ | $\log K^{Cu}_{CuL}$ | Ref. |
|---|---|---|---|
| | L = oxydiacetic acid | L = thiodiacetic acid | |
| $UO_2^{2+}$ | 5.11 | 3.16 | 19 |
| $VO_2^{2+}$ | 5.01 | 3.14 | 20 |
| $Ni^{2+}$ | 2.25 | 3.93 | 21 |
| $Al^{3+}$ | 3.16 | 1.93 | 22 |
| $Co^{2+}$ | 2.7 | 3.4 | 14 |
| $Zn^{2+}$ | 3.6 | 3.0 | 14 |
| $Ca^{2+}$ | 3.4 | 1.4 | 14 |
| $Cu^{2+}$ | 4.18 | 4.45 | [a] |

[a] This work.

### *Calculations*

The data relative to the formation constants of both binary and ternary systems were refined using the SCOGSB [9, 10] computer program. The standard deviation in titre was always less than 0.01 ml. The calculations relative to the protonation constants, the purity of the acids, the standard solution titre (potentiometrically determined) and the E° were performed using our ACBA [11] computer program. In the Tables our values are reported together with standard deviations.

## Results and Discussion

The proton association constants are reported in Table I together with the recently published literature values relative to the Se and Te derivatives [12, 13]. Our values are in agreement with those taken from the literature [14–17]; the trend for both $K^{H}_{HL}$ and $K^{HL}_{H_2L}$ falls in the order O > S > Se > Te in accordance with the decreasing electronegativity of the Group 6 atoms, going down the Group from oxygen to tellurium. The copper(II) complex formation constants are reported in Table II, together with those taken from the literature. This Table also includes Se derivatives [12]. Our values are in agreement with those published so far [14–18]; the constant for the $Cu(ODA)_2$ complex is reported here for the first time, as far as we know. Under our working conditions the formation of complexes like CuHL can never be neglected. Examining the $K^{Cu}_{CuL}$ constants as a function of the central donor atom we find that S > O > Se. This trend is the same as the one shown by the propionic acid derivatives, in which the central atom is believed to be bound [12]. In addition to the similarity of these acids with the propionic derivatives, there is other evidence to support the hypothesis of the coordination of the central donor atom.

As shown in Table III, the "hard" cations produce more stable complexes with ODA than with TDA, while the "soft" cations produce more stable complexes with TDA [19–22]. This behaviour can be attributed to the central atom coordination in accordance with the "hard" oxygen and the "soft" sulphur nature. In fact the stability constant of Cu–TDA is higher than that of CuODA. This behaviour is different from that observed for typically "hard" cations, whereas it is more similar to that of Ni and Co, for which a bond with the heteroatom has been found to exist. Besides the thermodynamic considerations, the spectroscopic results give further evidence to support the coordination of the central donor atom. In fact Rossotti *et al.* [23] affirm, on the basis of N.M.R. data, that the diglycollate appears to be bidentate, thus hypothesizing for the CuODA complex the coordination of the central atom and of one of the two carboxylic groups.

However, there is a discrepancy between Rossotti's hypothesis and the value of the stability constant of CuSucc ($\log K^{Cu}_{CuSucc}$ = 2.61, where Succ is succinic acid) [24] on one hand, and CuODA and CuTDA on the other hand. In fact $\log K^{Cu}_{CuL}$ for both CuODA and CuTDA is notably higher than that found for CuSucc; this would not occur if the ligand were not coordinated to three donor atoms because of the positive entropic contribution which is due to the neutralization of the cupric ion charge with the resulting formation of uncharged complexes in the ratio 1:1 as for the CuSucc system.

The high stability of the protonated MHL complexes supports chelate formation through the Group VI donor atoms.

In the presence of copper(II) and 2,2′-dipyridyl, TDA and ODA produce a neutral and a protonated species, Cu(dip)L and Cu(dip)HL, respectively. The neutral ternary complex is formed in appreciable amount also at relatively low pH. At the pH value corresponding to the $\log K^{H}_{HL}$ the formation percentages are 70 and 90 for ODA and TDA respectively, when these ligands are in excess with respect to the Cu(dip). The protonated complex which is formed in appreciable amount in the Cu(dip)ODA system is practically negligible in the Cu(dip)TDA system; in both cases the maximum amount found is reached at pH = 3. In Table IV the values of the equilibrium constants concerning the ternary systems are shown.

In Fig. 1 and 2 the distribution diagrams of formation *versus* pH for both ODA and TDA systems are shown. Comparing the formation constant values of the neutral ternary complexes investigated in this work with the one concerning the Cu(dip)Succ complex ($\log \beta_{11}$ = 10.90) [26], it seems reasonable to assume that also in the mixed complexes all the donor atoms are coordinated with the cupric ion. This hypothesis is based only on ΔG values, without taking into account any contrasting entropic and

TABLE IV. Formation Constants of Copper(II) Complexes with 2,2′-Dipyridyl and Oxydiacetic or Thiodiacetic Acids in Aqueous Solution at 25 °C and I = 0.1 *M* ($NaClO_4$).[a]

| L | $\log \beta^{Cu}_{Cu(dip)L}$ | $\log \beta^{Cu}_{Cu(dip)HL}$ | $\log K^{Cu(dip)}_{Cu(dip)L}$ | $\log K^{Cu(dip)}_{Cu(dip)HL}$ |
|---|---|---|---|---|
| Oxydiacetic acid | 11.64 ± 0.04 | 14 40 ± 0.15 | 3.53 ± 0.07 | 2.4 ± 0.2 |
| Thiodiacetic | 12.41 ± 0.01 | 14.0 ± 0.3 | 4.30 ± 0.04 | 1.8 ± 0.4 |

[a] $\beta^{Cu}_{Cu(dip)L}$ = [Cu(dip)L]/[Cu] [dip] [L]. $\beta^{Cu}_{Cu(dip)HL}$ = [Cu(dip)HL]/[Cu] [dip] [H] [L]. $K^{Cu(dip)}_{Cu(dip)L}$ = [Cu(dip)L]/[Cu(dip)] [L]. $K^{Cu(dip)}_{Cu(dip)HL}$ = [Cu(dip)HL]/[Cu(dip)] [HL].

TABLE V. Stabilization Parameters for the Ternary Complexes of Copper(II) with 2,2′-Dipyridyl and Some Tridentate Ligands in Aqueous Solution at 25 °C and I = 0.1 *M* ($NaClO_4$).

| Complex[a] | Δ logK[b] | Ref. |
|---|---|---|
| Cu(dip)IDA | −1.90 | 6 |
| Cu(dip)DIPIC | −1.30 | 6 |
| Cu(dip)ODA | −0.65 | c |
| Cu(dip)TDA | −0.15 | c |

[a] IDA = iminodiacetic acid. DIPIC = dipicolinic acid. [b] Δ log K = $\log \beta^{Cu}_{Cu(dip)L} - (\log K^{Cu}_{Cu(dip)} + \log K^{Cu}_{CuL})$. [c] This work.

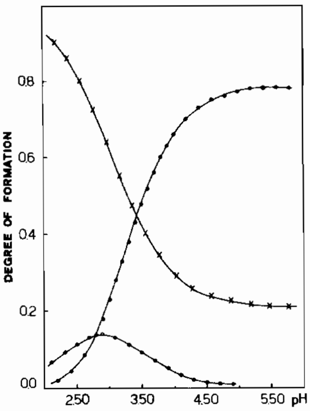

Figure 1. Distribution diagram, obtained with DISDI program [25], of the Cu(dip)ODA system. $[Cu]_T$ = $[dip]_T$ = 0.9 m*M*, $[ODA]_T$ = 1.8 m*M*. X Cu(dip); · Cu(dip)ODA; ○ Cu(dip)HODA.

enthalpic contributions or different structural contributions. Also for the ternary systems the stability is in the order S > O, but, in this case, the difference is bigger than that observed in the parent complexes (0.8 against 0.3 logarithmic unities). If we compare the copper perchlorate and the copper bound to the ligand (*i.e.* 2,2′-dipyridyl), provided both complexes have the same charge, the second one emphasizes the difference between the "softer" S-atom and the "harder" O-atom.

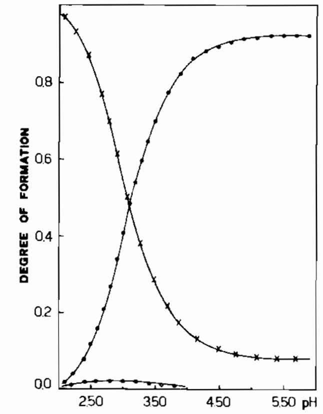

Figure 2. Distribution diagram, obtained with DISDI program [25], of the Cu(dip)TDA system. $[Cu]_T$ = $[dip]_T$ = 1 m*M*, $[TDA]_T$ = 1.5 m*M*. X Cu(dip); · Cu(dip)TDA; ○ Cu(dip)HTDA.

If we consider the Δ logK values, shown in Table V, other evidence supporting the coordination of the central atom (O, S) can be seen. As a first approximation, taking Δ logK as a measure of the ternary complex stabilization with respect to the binary complexes, thus disregarding the interaction with the solvent, the formation of the chromophore $N_2O_2S$ is more favoured than either $N_2O_3$ or $N_3O_2$, in spite of the higher stability of the Cu(dip)IDA (IDA = iminodiacetic acid) system with the complexes investigated in this work.

Recently Sigel [27] has calculated the Δ logK statistic value for ternary systems having two bidentate ligands; this author found that up to −0.9—−1.1 values the ternary complexes are more stabilized than the binary ones. In our systems in which there are present a bidentate and a tridentate ligand, one can assume that the Δ logK statistic value is even lower than −1.1; therefore the Cu(dip)ODA and Cu(dip)-TDA complexes are more stabilized with respect to the parent complexes.

## Acknowledgement

We thank C.N.R. (Rome) for support.

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