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# THERMODYNAMICS OF COPPER(II) 2,2′-DIPYRIDYL COMPLEXES IN AQUEOUS SOLUTION

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## ABSTRACT

The thermodynamic parameters for the chelation of cupric ion with 2,2′-dipyridyl have been redetermined at 25°C and $I = 0.1$ M. $\Delta G$ values were obtained by potentiometry with a selective ion electrode and $\Delta H$ values by direct calorimetry. Similar studies have been made on the relative hydroxocomplexes. The data obtained are compared with those in the literature and the chelate effect of the heterocyclic diimine is described.

## INTRODUCTION

Many workers have studied the formation of copper(II)-2,2′-dipyridyl complexes in aqueous solution and have also determined the thermodynamic functions of complex formation[1–9]. However, there is considerable disagreement among the values reported in the literature: for example, for CuDip (Dip = 2,2′-dipyridyl) complex the formation constants vary from 6.33 to 8.39 logarithmic unities and, the formation enthalpies, from—8.3 to—11.9 kcal $\text{mol}^{-1}$; these differences cannot be explained by the different experimental conditions.

For some years the study of copper(II) with 2,2′-dipyridyl mixed complexes has been in progress in our laboratory[10–14]. We believed it necessary to determine again the $\Delta G$ and $\Delta H$ values for this system by appropriate experimental techniques under the same conditions of ionic strength and temperature previously used by us. As there is also disagreement on the kind of the hydrolytic species formed at pHs higher than 5[1,15–17], we have carried out a study on the formation of the hydroxocomplexes and determined the relative $\Delta G$ and $\Delta H$ values.

The formation constants have been determined potentiometrically, by using a glass electrode or a copper-sensitive electrode; the relative enthalpic changes have been determined calorimetrically.

## EXPERIMENTAL

### *Reagents and solutions*

The 2,2′-dipyridyl (C. Erba RP) was recrystallized from water–ethanol before use. The standard solutions were prepared and standardized as previously described[10,13,18]. All the solutions were prepared with carbon-dioxide-free bidistilled water and were led at ionic strength 0.1 M by adding $NaClO_4$ or $NaNO_3$.

*Potentiometric measurements*

The pH-metric measurements were performed by using Ingold's and Radiometer's pairs of glass-saturated calomel electrodes. The free copper concentration was measured out by using a copper(II) sensitive electrode. This kind of electrode has been developed in the last years and widely employed to determine the formation constants[9,19–21]. We have used an Amel sens-ion Model 201 Cu electrode with Ingold's reference electrode. The potentials were measured by means of an Orion Model 801 A potentiometer. The kind of response of this electrode was also widely studied by us, and, as an example, in Table 1 is reported a calibration from which the $E^\circ$ constancy is outstanding. The response time for $p$Cu lower than 5 is about 2–10 min, but it rapidily increases until it becomes about 1 h at higher $p$Cu.

TABLE 1

DETERMINATION OF Cu (II)-SELECTIVE ELECTRODE $E^\circ$ BY ADDING $T_1$ TO 50 ml OF 0.1 M $NaNO_3$ SOLUTION
$T_1 = Cu(NO_3)_2$ 0.410 mM, $NaNO_3$ 0.1 M

| *v (ml)* | *E (mV)* | *p*Cu | *E° (mV)* |
|---|---|---|---|
| 1.00 | 144.8 | 5.095 | 295.5 |
| 2.00 | 153.7 | 4.802 | 295.7 |
| 3.50 | 160.6 | 4.571 | 295.8 |
| 5.00 | 165.0 | 4.429 | 295.9 |
| 7.00 | 168.9 | 4.298 | 295.9 |
| 9.00 | 171.5 | 4.204 | 295.8 |
| 11.00 | 173.6 | 4.131 | 295.8 |
| 13.00 | 175.3 | 4.073 | 295.7 |
| 15.00 | 176.7 | 4.024 | 295.7 |
| 17.00 | 178.0 | 3.983 | 295.8 |
| 19.00 | 179.1 | 3.947 | 295.8 |
| 21.00 | 180.0 | 3.916 | 295.8 |
| 23.00 | 180.8 | 3.889 | 295.8 |
| 25.00 | 181.6 | 3.864 | 295.9 |
| | | | $E^\circ = 295.8 \pm 0.1$ |

As regards the binary complexes, the measurements were performed by adding partially protonated dipyridyl to a cupric ion solution and vice versa. The analytical concentrations of the reagents varied from 0.5 to 2 mM and the ratio $[Dip]_T/[Cu]_T$ in the range 1–4.

The measurements on CuDip hydrolysis have been performed by adding sodium hydroxide to a solution having $[Cu]_T = [Dip]_T = 1$ mM. The titrant was added by means of Metrhom Multidosimat E 415 burette. The temperature was kept constant at the value of $25 \pm 0.1$ °C by pumping thermostated water through the mantle of the vessel; magnetic stirring was employed.

*Calorimetric measurements*

The experimental apparatus, the measurement technique and the calorimeter have been previously described[18].

The enthalpy of 2,2'-dipyridyl protonation was obtained by titrating 1–4 mM $HClO_4$ with 9–12 mM 2,2'-dipyridyl (partially protonated) or 10 mM 2,2'-dipyridyl (partially protonated) with 100 mM $HClO_4$. The enthalpies of the complexes and the hydroxocomplexes were obtained by titrating 2.5–0.5 mM $Cu(ClO_4)_2$ or $Cu(ClO_4)_2$, 2,2'-dipyridyl and 1 mM $HClO_4$ with 15 mM 2,2'-dipyridyl (partially protonated) or 100 mM NaOH, respectively.

### *Calculations*

The formation constants of the $Cu(Dip)_n^{2+}$ complexes have been calculated by means of the computer program MINIQUAD[22] and the hydrolysis constants by means of the program SCOGSB[13,23]. The enthalpies of formation have been calculated by means of the program DOEC[24]. Other details of our calculations methods have been previously reported[13,18].

## RESULTS

### *Equilibrium constants*

In Table 2 we report the logarithmic values of the formation constants of the $Cu(Dip)_n^{2+}$ complexes together with the literature values. One can note that our

TABLE 2

STABILITY CONSTANTS OF Cu (II)-2,2'-dipyridyl COMPLEXES

| *Medium (M)* | *Temp. (°C)* | $pK_a$ | *n* | *log* $K_n$ | *log* $\beta_n$ | *Method*[a] | *Ref.* |
|---|---|---|---|---|---|---|---|
| 0.1 $NaClO_4$ | 25 | — | 1 | 6.44 | — | gl | 3 |
| | | | 2 | 5.74 | 12.18 | | |
| 0.1 $NaNO_3$ | 20 | 4.49 | 1 | 8.0 | — | gl, Hg | 5 |
| | | | 2 | 5.60 | 13.60 | | |
| 0.3 $K_2SO_4$ | 25 | 4.50 | 2 | 5.60 | — | gl, Pt | 2 |
| | | | 3 | 3.20 | — | | |
| 0.1 KCl | 25 | 4.47 | 1 | 8.15 | — | dis | 4 |
| | | | 2 | 5.50 | 13.65 | | |
| | | | 3 | 3.30 | 16.96 | | |
| 1 $KNO_3$ | 30.3 | 4.62 | 1 | 8.39 | — | gl | 7 |
| | | | 2 | 5.63 | 14.02 | | |
| | | | 3 | 3.63 | 17.65 | | |
| 0.1 $KNO_3$ | 25 | — | 1 | 6.33 | — | gl | 1 |
| 0.1 $NaClO_4$ | 25 | — | 1 | 8.11 | — | gl[b] | 14 |
| 1 $NaClO_4$ | 25 | — | 1 | ~8.5 | — | dis | 8 |
| 1 $KNO_3$ | 25 | — | 1 | ~8.2 | — | dis | 8 |
| 0.1 $KNO_3$ | 25 | — | 2 | — | 13.65 | CSE[c] | 9 |
| | | | 3 | — | 16.75 | | |
| 0.1[d] | 25 | 4.463(5) | 1 | 8.11(2) | — | gl, CSE[c] | this work[e] |
| | | | 2 | 5.55(3) | 13.66(3) | | |
| | | | 3 | 3.39(15) | 17.05(15) | | |

[a] Refs. 36 and 37. [b] In solutions containing a second ligand (iminodiacetic acid). [c] CSE = copper(II) selective electrode. [d] $[NaNO_3]/[NaClO_4] = 0.25$ to 4. [e] The figures in parentheses are the standard deviations in the last decimal figure.

values are in agreement with those determined by techniques different from the pH-metric method. In fact it stands to reason that this technique cannot be used for the determination of the first constant, because also at a low pH the $CuDip^{2+}$ complex is almost completely formed and so there is not any competition between the cupric ion and proton.

Particularly, the values of the formation constants reported by Anderegg[5], and Irving and Mellor[4] are very similar to ours. As regards Anderegg's value of the first constant we obtained, by applying Van 't Hoff's equation, at 25°C, $\log K_1 = 8.13 \pm 0.05$ and as regards that of Irving and Mellor, by repeating the calculations with the aid of the least-squares method $\log K_1 = 8.14 \pm 0.04$. These values are therefore in agreement (it is unusual to find values of formation constants determined by means of three different techniques in literature, which differ more than 0.03 logarithmic unities) and Bauman's[25] argumentations on the supposed superiority of the pH-metric method also for these systems have to be rejected.

TABLE 3

HYDROLYSIS CONSTANTS OF Cu(2,2′-dipyridyl)

| *Medium (M)* | *Temp. (°C)* | *pq* | $-\log^* K_{pq}$ | $\log^* \beta_{pq}$ | $\log K_{pq}$ | $\log K_d$ | *Ref.* |
|---|---|---|---|---|---|---|---|
| 0.1 $KNO_3$ | 25 | 11 | 8.7 | — | — | — | 16 |
| | | 22 | 10.74 | — | — | 6.7 | |
| | | 12 | 16.28 | — | — | — | |
| 0.1 $KNO_3$ | 25 | 11 | — | — | 6.6 | — | 15 |
| 0.1 $KNO_3$ | 25 | 11 | 7.9 | — | — | — | 1 |
| | | 22 | 10.81 | — | — | 5.0 | |
| | | 12 | 17.67 | — | — | — | |
| 0.1 $KNO_3$ | 20 | 22 | 11.06 | — | — | — | 17 |
| 0.1[a] | 25 | 11 | 7.70(15) | — | — | — | this work[b] |
| | | 22 | 10.60(5) | 5.62(5) | 16.8(1) | 4.80(15) | |
| | | 12 | (~17.5) | (~−9.4) | (~9.9) | — | |

$^*K_{pq}$: $p\,CuDip + q\,H_2O = Cu_pDip_p(OH)_q + qH$
$^*\beta_{pq}$: $p\,Cu + p\,Dip + q\,H_2O = Cu_pDip_p(OH)_q + qH$
$K_{pq}$: $p\,CuDip + q\,OH = Cu_pDip_p(OH)_q$
[a] $[NaNO_3]/[NaClO_4] = 0.25$ to 4. [b] The figures in parentheses are the standard deviations in the last decimal figure. The charges are omitted for simplicity.

In Table 3 are reported the values of $Cu(Dip)^{2+}$ hydrolysis constants with those of the literature. Martell et al.[1,15] and Ryland et al.[16] confirmed the formation of a monomeric species, $CuDip(OH)^+$, of a dimeric species, $Cu_2(Dip)_2(OH)_2^{2+}$, and of a neutral species, $Cu(Dip)(OH)_2$, while Perrin and Sharma[17] found only the dimeric species. We have found both the monomeric and dimeric species to be present, but it has not been possible either to verify or to exclude the existence of neutral species, although Hamilton's[26,27] test and a pseudo F-test[28] have been applied to the experimental data.

Our values are in good agreement with those of Gustafson and Martell. Perrin and Sharma value for $\log^* K_{22}$, i.e., −11.06, is not very different from ours, i.e.,

−10.60, because, although these authors have neglected the presence of the monomeric species, this is formed in such small quantities that they do not change considerably the hydrolysis constant of the dimeric species. This can easily be seen from Fig. 1 where the distribution diagram of the hydrolytic species against pH is plotted.

### *Enthalpies of formation*

In Table 4 the values of the formation enthalpies of the $Cu(Dip)_n^{2+}$ complexes determined in this work, those of the literature and the protonation enthalpies are

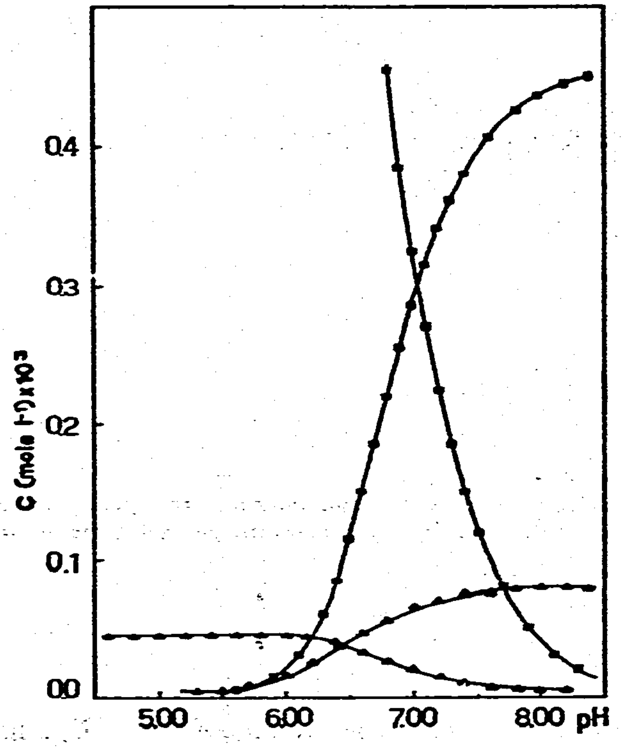

Fig. 1. Distribution diagram of the species present in aqueous solutions where: $[Cu]_T = [2,2'\text{-dipyridyl}]_T = 1$ mM at 25°C and $I = 0.1$ M. □, CuDip; ▲, $CuDip_2$; ■, $Cu_2Dip_2(OH)_2$; and △, CuDip(OH).

TABLE 4

$\Delta H^a$ VALUES FOR Cu(2,2′-dipyridyl)$_n$ COMPLEXES

| *Medium (M)* | *Temp. (°C)* | $-\Delta H_{K_H}$ | $-\Delta H_{\beta_1}$ | $-\Delta H_{\beta_2}$ | $-\Delta H_{\beta_3}$ | *Ref.* |
|---|---|---|---|---|---|---|
| 1 $NaClO_4$ | 25 | — | 8.3 | 16.6 | — | 3 |
| 0.1 $NaNO_3$ | 20 | 3.66 | 11.9 | 17.3 | 23.8 | 5 |
| 1 $KNO_3$ | 30.3 | 4.02 | 10.16 | 19.02 | 21.62 | 7 |
| 0.1$^b$ | 25 | 3.46(1) | 10.65(5) | 16.74(12) | 24.6(3) | this work$^c$ |

$^a$ ΔH values are in kcal $mol^{-1}$. $^b$ $[NaNO_3]/[NaClO_4] = 0.25$ to 4. $^c$ The figures in parentheses are the standard deviations in the last decimal figure.

reported. The values, as one can see, are very different and, particularly, $\Delta H_1$ reported by Baumann et al.[3] must certainly be considered too low; this is attributable to the fact that it has been determined by the method of potentiometric data temperature dependence, which gives results less reliable than those of the direct calorimetric method.

In Table 5 the hydrolysis $\Delta H$ values of $Cu(Dip)^{2+}$ with literature data are reported. It has to be pointed out that ours are the first values determined by direct calorimetry, the results of which, as already said, are more reliable than those obtained from temperature dependence of potentiometric data, in the case of multistage equilibria[29].

TABLE 5

$\Delta H^{a}$ VALUES FOR THE HYDROLYSIS OF Cu(2,2′-dipyridyl) AT 25°C

| *Medium (M)* | *pq* | $\Delta H_{*pq}$ | *Ref.* |
|---|---|---|---|
| 0.1 $KNO_3$ | 11 | 8 | 1[b] |
| | 22 | 12.9 | |
| 0.1 $KNO_3$ | 11 | 5.4 | 16[b] |
| | 22 | 8.2 | |
| 0.1[c] | 11 | 4.2(9) | this work[d] |
| | 22 | 16.4(5) | |
| | 12 | ~15 | |

[a] $\Delta H$ values are expressed in kcal $mol^{-1}$. [b] $\Delta H$ values were obtained from temperature dependence of potentiometric data. [c] $[NaNO_3]/[NaClO_4] = 0.25$ to 4. [d] The figures in parentheses are the standard deviations in the last decimal figure.

## DISCUSSION

In Table 6 the values of the equilibrium constants as well as of $\Delta G$, $\Delta H$, and $\Delta S$ for the reaction studied in this work are reported; the complexes $Cu(Dip)_n^{2+}$ are stabilized by a favorable enthalpy change. By a comparison with the 1,10-phenanthroline[30] it is possible to see that the enthalpy changes, due to the copper(II) complex formation, are very similar, whereas the entropie changes are different, and, more exactly, they are less positive for the $Cu(Dip)_n^{2+}$ complexes. This can be explained with the lesser amount of rigidity of 2,2′-dipyridyl.

The conclusions on the chelate effect[31,32] drawn by some authors[30,33] disagree with the similar thermodynamic behaviour of the two heterocyclic diimines. Eatough[30], in fact, points out that, unlike 2,2′-dipyridyl, in the case of 1,10-phenanthroline, the chelate stabilization is due to favourable enthalpy changes. The results reported in Table 7, however, show that, by using our data, also for the 2,2′-dipyridyl the chelate stabilization is substantially like that shown by 1,10-phenanthroline. The use of erroneous data explains the differences in the enthalpy change of the chelate stabilization.

TABLE 6

THERMODYNAMIC PROPERTIES FOR SIMPLE AND HYDROXYL Cu(2,2'-dipyridyl) COMPLEXES IN 0.1 M ($NaNO_3$-$NaClO_4$) AT 25°C

The charges are omitted for simplicity.

| *Reaction* | *log K* | $\Delta G$ (*kcal mol*$^{-1}$) | $\Delta H$ (*kcal mol*$^{-1}$) | $\Delta S$ (*cal deg*$^{-1}$ *mol*$^{-1}$) |
|---|---|---|---|---|
| $\mathrm{H + Dip = HDip}$ | 4.46 | −6.08 | −3.46 | 8.79 |
| $\mathrm{Cu + Dip = CuDip}$ | 8.11 | −11.05 | −10.65 | 1.3 |
| $\mathrm{CuDip + Dip = CuDip_2}$ | 5.55 | −7.57 | −6.09 | 5.0 |
| $\mathrm{Cu + 2Dip = CuDip_2}$ | 13.66 | −18.62 | −16.74 | 6.3 |
| $\mathrm{CuDip_2 + Dip = CuDip_3}$ | 3.4 | −4.6 | −7.9 | −11.0 |
| $\mathrm{Cu + 3Dip = CuDip_3}$ | 17.05 | −23.2 | −24.6 | −4.7 |
| $\mathrm{Cu + Dip + OH = CuDip(OH)}$ | 14.1 | −19.2 | −20 | −3 |
| $\mathrm{CuDip + OH = CuDip(OH)}$ | 6.0 | −8.2 | −9 | −3 |
| $\mathrm{2Cu + 2Dip + 2OH = Cu_2Dip_2(OH)_2}$ | 33.1 | −45.1 | −31.8 | 44.6 |
| $\mathrm{2CuDip + 2OH = Cu_2Dip_2(OH)_2}$ | 16.9 | −23.0 | −10.5 | 41.9 |
| $\mathrm{Cu + Dip + H_2O = CuDip(OH) + H}$ | 0.4 | −0.6 | −6.5 | −20 |
| $\mathrm{CuDip + H_2O = CuDip(OH) + H}$ | −7.7 | 10.5 | 4.2 | −21 |
| $\mathrm{2Cu + 2Dip + 2H_2O = Cu_2Dip_2(OH)_2 + 2H}$ | 5.65 | −7.70 | −4.9 | 9.4 |
| $\mathrm{2CuDip + 2H_2O = Cu_2Dip_2(OH)_2 + 2H}$ | −10.6 | 14.5 | 16.4 | 6.4 |
| $\mathrm{2CuDipOH = Cu_2Dip_2(OH)_2}$ | 4.9 | −6.7 | 8 | 49 |

TABLE 7

CHELATE EFFECT FOR 2,2′-dipyridyl

| | $\Delta G^a$ (*kcal mol$^{-1}$*) | $\Delta H^b$ (*kcal mol$^{-1}$*) | $\Delta S$ (*cal deg$^{-1}$ mol$^{-1}$*) | $\Delta G'^c$ | $\Delta H'^c$ | $\Delta S'^c$ |
|---|---|---|---|---|---|---|
| CuPy$_2$ + Dip = CuDip + 2Py | −5.05 | −1.9 | 10.6 | −2.7 | −1.9 | 2.7 |
| | (−3.46)$^d$ | (−2.43)$^d$ | (3.4)$^d$ | (−1.10)$^d$ | (−2.43)$^d$ | (−4.5)$^d$ |
| | | | | (−1.2)$^e$ | (0.5)$^e$ | (5.7)$^e$ |
| CuPy$_4$ + 2Dip = CuDip$_2$ + 4Py | −9.7 | 2.3 | 40 | −7.3 | 3.2 | 32 |
| | (−8.41)$^d$ | (−4.86$^d$) | (11.9)$^d$ | (−3.69)$^d$ | (−4.86)$^d$ | (−3.9)$^d$ |
| | | | | (−4.3)$^e$ | (4.7)$^e$ | (30)$^e$ |

[a] Refs. 36 and 37: $Cu^{2+}$-Py system. [b] Refs. 34 and 35: $Cu^{2+}$-Py system. [c] Ref. 32: $CuPy_{2j} + j\text{Dip} = CuDip_j + 2j\text{Py}$; $\Delta G'_j = \Delta G_j + jRT \ln 55.5$; $\Delta H'_j = \Delta H_j$; $\Delta S'_j = \Delta S_j - jR \ln 55.5$. [d] Ref. 33. [e] Ref. 30.

As regards the free energy, pertinent to the formation of $CuDip(OH)^+$ and $Cu_2Dip_2(OH)_2^{2+}$ hydrolytic species, it has to be pointed out that they are surprisingly similar to those of $Cu(OH)^+$ and $Cu_2(OH)_2^{2+}$ previously reported[18].

Recent X-ray studies[38] in aqueous solution on $Cu(ClO_4)_2$ showed that the cupric ion is surrounded by four water molecules in the equatorial sites at a distance of 1.94 Å and by two others in the axial sites at a distance of 2.43 Å. The structure assumed for the monomeric and dimeric species by many authors does not give any information on the other two disposable positions (axial ones). This is of great importance if the entropic and enthalpic changes pertinent to the equations summarized in Table 8 are taken into consideration, also taking into account the considerable uncertainty of some of them. Particularly the $CuDip(OH)^+$ dimerization is considerably more endothermic than that of $Cu(OH)^+$ and it is also stabilized by doubled entropic change. It would seem that in the first case a larger number of bonds are broken and tentatively it might be supposed that also the water molecules in the axial sites are removed. The entropy change would also be produced by the ring-chelate formation and also by the removal of the axial water molecules.

TABLE 8

COMPARISON OF THERMODYNAMIC DATA FOR HYDROLYZED SPECIES RELATIVE TO $Cu(H_2O)_6$ AND $CuDip(H_2O)_4$

The charges are omitted for simplicity.

| | *log K* | $\Delta H$ (*kcal mol*$^{-1}$) | $\Delta S$ (*cal deg*$^{-1}$ *mol*$^{-1}$) |
|---|---|---|---|
| $Cu + OH = CuOH$ | 6.00 | −5.0 | 11 |
| $CuDip + OH = CuDipOH$ | 6.00 | −9 | −3 |
| $2Cu + 2OH = Cu_2(OH)_2$ | 16.69 | −8.5 | 48 |
| $2CuDip + 2OH = Cu_2Dip_2(OH)_2$ | 16.9 | −10.5 | 41.9 |
| $2CuOH = Cu_2(OH)_2$ | 4.69 | 2 | 26 |
| $2CuDipOH = Cu_2DiP_2(OH)_2$ | 3.9 | 8 | 49 |

Recently, Majeste and Meyers[39] have determined, by X-ray diffraction on a single crystal, the bis-Dip-dihydroxocopper(II) nitrate structure. In their work, it has been verified that the cupric ion has a tetragonal pyramidal arrangement lightly distorted. The copper is bonded in the equatorial plain with the Dip nitrogen atoms at a distance of 2.00 Å and with the hydroxilic oxygen atoms at 1.92 Å, whereas along the z-axis it is bonded to the nitrate group at a distance of 2.379 Å. Considering the differences between the solid state and the solution, it is interesting to note the absence of water molecules, even if one of the five coordinating sites is occupied by the oxygen of the nitrate group.

Also as regards the monomeric species formation, $\Delta G$ being equal, there are different values of $\Delta H$ and $\Delta S$. We think the positive value of $\Delta S$ for $Cu(OH)^+$ species is due to the partial neutralization of the cupric ion charge, unlike the $CuDip^{2+}$

ion, where the existence of the 2,2′-dipyridyl $\pi$ system allows a new distribution charge of the metal, which seems to be more positive.

Further determinations of thermodynamic functions involved in the copper(II) hydrolytic processes would better explain the behaviour of the olation reactions founded till now on $\Delta G$ measurements.

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