the theoretical predictions and the known chemical properties of the complexes, especially for silver porphyrins. The following reduction schemes account for these experimental observations.

$$\mathrm{Ag^{II}P} + e^- \rightleftarrows \underset{\text{unstable}}{[\mathrm{Ag^{I}P}]^-} \xrightarrow[\mathrm{(H^+)}]{\text{demetalation}} \mathrm{Ag^+ + H_2P}$$

$$[\mathrm{Tl^{III}P}]^+ + 2e^- \rightarrow \underset{\text{unstable}}{[\mathrm{Tl^{I}P}]^-} \xrightarrow[\mathrm{(H^+)}]{\text{demetalation}} \mathrm{Tl^+ + H_2P}$$

$$\mathrm{P = TPP,\ TPP(CN)_4,\ OEP}$$

Even careful purification of the solvent and electrolytes used in the experiments leaves traces of water or other impurities able to generate protons.[27]

Registry No. $\mathrm{Ag^{II}TPP}$, 14641-64-6; $\mathrm{Ag^{II}TPP(CN)_4}$, 57948-05-7; $\mathrm{Ag^{II}OEP}$, 36609-71-9; $\mathrm{Tl^{III}TPP(OCOCF_3)}$, 76011-09-1; $\mathrm{Tl^{III}OEP(OCOCF_3)}$, 51436-47-6; $\mathrm{H_2TPP}$, 917-23-7; $\mathrm{H_2OEP}$, 2683-82-1; $\mathrm{H_2TPP(CN)_4}$, 52353-92-1.

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Mixed-Metal Complexes in Solution. 3. Thermodynamic Study of Heterobinuclear Copper(II)-L-Histidine and -Histamine Complexes in Aqueous Solution

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Potentiometric measurements have been used to characterize the equilibrium system containing copper(II), L-histidine (his) or histamine (hm), and M (M = $\mathrm{Ni^{II}}$, $\mathrm{Zn^{II}}$, or $\mathrm{Cd^{II}}$). The results obtained provide evidence for heterobinuclear species containing $\mathrm{Cu^{II}}$, M, and his or hm. The thermodynamic parameters of these complexes were determined by direct calorimetry. Some hypotheses for the structures of $\mathrm{[CuM(his)_2]^{2+}}$ and $\mathrm{[CuM(hm)_2]^{4+}}$ are discussed.

Introduction

In previous papers,[2,3] we reported the stability constants in aqueous solution of heteronuclear complexes formed by polyfunctional ligands such as L-histidinate or citrate with two different transition-metal ions. While quite a few qualitative studies can be found in the literature, as far as we know just some ten values of stability constants determined in aqueous solution, in addition to those reported by us, are available.[4-8] An attempt has been made to characterize the equilibrium systems and to determine the framework of a structure of some heterobinuclear species; unfortunately this EPR investigation,[9] carried out in nonaqueous solution, did not allow the authors to draw any definitive conclusions on the arrangement of the ligand around the metal ions. Considering that the thermodynamic parameters can give useful information on the bonding details, as shown for simple complexes[10-12] and for complexes containing two different ligands,[12-16] we thought it interesting to determine, by direct calorimetry, the heats of formation of the heteronuclear complexes and to calculate their $\Delta H°$ and $\Delta S°$ values.

Table I. Experimental Details of Potentiometric Measurements for Complex Formation at 25 °C and I = 0.1 mol dm^{-3} ($\mathrm{KNO_3}$)[a]

M	c_{Cu}	c_{M}	$c_{\mathrm{H_2L}}$	no. of points	pH range
$\mathrm{Zn^{2+}}$	3.5	7	3.5	35	3-7.3
	4	8	4	25	3-7.3
	3	6	3	24	3-7.3
	3	15	6	26	3-7.3
	4	12	8	28	3-7.3
	3	6	9	33	3-7.3
	5	6	7	41	7.3
$\mathrm{Cd^{2+}}$	3	9	6	26	3-7.8
	3	15	6	27	3-7.8
	3	6	3	23	3-7.8
	4	6	4	29	3-7.8
	3	5	3	24	3-7.8
	3	6	9	31	3-7.8
	5	6	7	28	3-7.8
		3	10	45	5-10
		2.5	10	40	3-10
		4	12	39	3-10
		3.5	15	42	3-10
		4	4	20	5-6.5
		3	6	35	5-9
$\mathrm{Ni^{2+}}$	4	6	3.8	27	3.0-7.5
	3	6	3	28	3.0-7.5
	3	4	3	31	3.0-7.5
	3	15	6	26	3.0-7.5
	2.5	15	4.8	23	3.0-7.5
	4	8	4	33	3.0-7.5
	3	6	9	30	3.0-7.5
	5	6	7	27	3.0-7.5

[a] The concentrations are expressed in mmol dm^{-3}.

We investigated the ternary complexes of L-histidinate (his) and histamine (hm) with all the possible pairs formed by the $\mathrm{Cu^{II}}$, $\mathrm{Zn^{II}}$, $\mathrm{Ni^{II}}$, and $\mathrm{Cd^{II}}$ ions. Histamine forms heteronuclear complexes with copper(II)-zinc(II) and copper(II)-cadmi-

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um(II) only. We were not able to determine stability constants for L-histidine complexes other than those previously reported.[2] The thermodynamic data here obtained are compared with those of the corresponding simple parent complexes determined by us under the same experimental conditions ($I = 0.1$ mol dm^{-3} (KNO$_3$) and $t = 25$ °C).

It was necessary to determine the stability constants of the binary complexes of Cd^{II} with histamine, since the literature data obtained under similar experimental conditions were not complete.

Experimental Section

Chemicals. L-Histidine (Aldrich) and histamine (Fluka) were used without further purification. Their purity was checked by (i) titration with CO$_2$-free standard KOH (in all cases a value higher than 99.7% was found) and (ii) determination of the p*K*s (the values found were in agreement with those previously determined[17] within 0.02 logarithmic units). Metal nitrate stock solutions were prepared and standardized as previously reported.[18] All the standard solutions were prepared by using twice-distilled water; their ionic strength was kept at 0.1 mol dm^{-3} by adding KNO$_3$.

Emf Measurements. The potentiometric measurements were carried out by means of either an Orion potentiometer (Model 801A, using an EIL glass electrode and an Ingold 303 NS calomel electrode) or a Metrohm potentiometer (Model E 600, equipped with glass and calomel electrodes supplied by the same firm). The calibration of the glass electrodes both in acidic and alkaline regions as well as other details were as previously described.[18] A Radiometer Selectrode (Model F 1112 Cu) and a copper amalgam electrode were also employed. Table I shows the experimental conditions of the alkalimetric titrations for both simple and mixed complexes.

Calorimetric Measurements. The calorimetric measurements were carried out at 25 ± 0.001 °C by employing a LKB precision calorimeter (Model 8700) and a 100-mL titration vessel (Model 8726-1). The reproducibility of the system and other details have already been reported.[19] In order to measure the formation heats of the simple and mixed complexes, we carried out at least seven calorimetric titrations for each system. The measurements were performed with use of, in turn, as titrant, the ligand or a solution containing one metal ion or a solution containing both metal ions in suitable ratios. Experimental details of the calorimetric measurements are reported in Table II.

Data Analysis and Calculations. The data considered in the calculations were only those obtained by measurements of hydrogen ion concentration with glass electrodes. In fact, attempts to measure the copper(II) ion concentration, which could be a confirmation of heteronuclear complex formations, failed. With the copper amalgam electrode stable emf values could not be obtained, probably owing to ligand decomposition processes, involving also different oxidation states of the metal ion. We faced some trouble, unconnected with the presence of other metal ions, also when an ion-selective electrode was used; in this case, though, the qualitative emf trend was what one would have expected, hypothesizing the formation of heteronuclear complexes.

The existence of ternary binuclear complexes in solution was inferred from the comparison between the experimental alkalimetric titration curves and the ones calculated by taking into account all the binary species only. At the same pH, there was a significant difference between experimental and calculated values of alkali concentration, thus indicating that heteronuclear species were likely to exist.

In order to determine the type of such heterobinuclear complexes, we examined the trend of the alkalimetric titration curves that exhibit two buffer regions, one at low pH and the other in the neutral pH range (this second buffered region is small, owing to the precipitation occurring above pH 7.5). The complexes formed and their stability constants were at first studied by means of a graphical method[20] that is outlined below.

Table II. Experimental Details of Calorimetric Measurements for Complex Formation at 25 °C and $I = 0.1$ mol dm^{-3} (KNO$_3$)

	titration vessel[a]					
M	C_{Cu}	C_M	C_L	C_H	titrant[a]	no. of points
			L = histidine			
Ni^{2+}		0	15.0	2.3	Ni^{2+} 50.05	14
		0	13.1	7.0	Ni^{2+} 50.05	13
		0	22.0	1.1	Ni^{2+} 50.05	17
		0	28.7	0.5	Ni^{2+} 50.05	11
	0	14.7	22.9	2.12	Cu^{2+} 123.8	15
	0	14.7	22.9	9.20	Cu^{2+} 123.8	11
	4.0	7.5	0	0.05	his$^-$ 35.3, H$^+$ 7.1	15
	2.9	4.9	0	0.05	his$^-$ 35.3, H$^+$ 7.1	15
	3.0	4.5	0	0.05	his$^-$ 35.3, H$^+$ 7.1	15
	0	0	15.0	0	Cu^{2+} 40.00, Ni^{2+} 70.00	16
	0	0	15.0	−2.9	Cu^{2+} 40.00, Ni^{2+} 70.00	13
Zn^{2+}	0	15.0	23.0	2.2	Cu^{2+} 123.8	14
	0	15.0	23.0	9.4	Cu^{2+} 123.8	11
	0	31.0	25.0	17.0	Cu^{2+} 123.8	7
	0	31.0	25.0	14.5	Cu^{2+} 123.8	14
	0	0	15.0	0.5	Cu^{2+} 40.0, Zn^{2+} 73.5	15
	0	0	20.0	0.5	Cu^{2+} 40.0, Zn^{2+} 73.5	15
Cd^{2+}		0	13.7	13.7	Cd^{2+} 77.0, H$^+$ 5.0	15
		0	10.0	6.0	Cd^{2+} 77.0, H$^+$ 5.0	16
		0	14.0	3.0	Cd^{2+} 77.0, H$^+$ 5.0	20
		0	25.3	4.0	Cd^{2+} 77.0, H$^+$ 5.0	17
	0	15.4	23.0	2.4	Cu^{2+} 123.8	15
	0	15.4	23.0	9.2	Cu^{2+} 123.8	12
	0	31.0	25.0	17.0	Cu^{2+} 125.0	13
	0	31.0	25.0	15.0	Cu^{2+} 125.0	7
	0	0	20.5	2.1	Cu^{2+} 40.0, Cd^{2+} 71.4	14
			L = histamine			
Zn^{2+}	0	31.0	25.0	15.0	Cu^{2+} 125.0	12
	0	43.0	30.0	18.0	Cu^{2+} 125.0	13
	0	25.4	31.6	9.3	Cu^{2+} 125.0	16
	0	0	21.4	2.1	Cu^{2+} 50.0, Zn^{2+} 70.5	11
	0	0	27.0	4.0	Cu^{2+} 50.0, Zn^{2+} 70.5	12
Cd^{2+}	0	30.0	25.0	15.0	Cu^{2+} 125.0	11
	0	41.0	30.0	18.0	Cu^{2+} 125.0	13
	0	27.0	29.5	6.9	Cu^{2+} 125.0	17
	0	0	27.1	8.0	Cu^{2+} 40.0, Cu^{2+} 71.4	11
	0	0	26.4	5.3	Cu^{2+} 40.0, Cu^{2+} 71.4	12
		0	35.0	14.0	Cd^{2+} 148.0	16
		0	37.0	6.5	Cd^{2+} 148.0	16
		0	27.2	15.9	Cd^{2+} 148.0	16
		0	41.3	8.4	Cd^{2+} 148.0	14

[a] The concentrations are expressed in mmol dm^{-3}.

Let us assume that M^{II}, M$^{II\prime}$, L, and H$^+$ (L = ligand) are the components G_1, G_2, G_3, and G_4, respectively. The generic species S_j can be expressed by reaction 1, where p_{ji} are the stoichiometric coefficients.

$$p_{j1}G_1 + p_{j2}G_2 + \ldots + p_{j4}G_4 \rightleftarrows S_j\ (\equiv S_{(p_{j1},\ldots,p_{j4})}) \tag{1}$$

Then, with c_i and s_j being the free concentration of the *i*th component and of the *j*th species, β of the *j*th species will be

$$\beta_j = s_j / \prod_i c_i^{p_{ji}} \tag{2}$$

The mass balance equation of the *i*th component, in the most general terms, can be expressed by

$$C_i = c_i + \sum_j p_{ji} s_j \tag{3}$$

where C_i is the total concentration. This, if $c_i = s_0$, can be written as

$$C_i = \sum_j p_{ji} s_j \tag{4}$$

For a fixed value of j, i.e., $j = j'$

$$C_i = [\sum_j p_{ji}(\beta_j \prod_i c_i^{p_{ji}})]_{j \neq j'} + [p_{ji}(\beta_j \prod_i c_i^{p_{ji}})]_{j = j'} \tag{5}$$

and

$$p_{j'i}\beta_{j'} = C_i - [\sum_j p_{ji}(\beta_j \prod_i c_i^{p_{ji}})]_{j \neq j'} [\prod_i c_i^{p_{ji}}]_{j = j'}^{-1} \tag{6}$$

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Table III. Thermodynamic Parameters for Proton-, Copper(II)-, Zinc(II)-L-Histidine and -Histamine Complexes at 25 °C and $I = 0.1$ mol dm^{-1} (KNO_3)[a]

reaction	$-\Delta G°$ [b]	$-\Delta H°$ [c]	$\Delta S°$ [c]
$H + his \rightleftarrows [H(his)]$	12.40	10.53 (5)[d]	6.3 (2)
$2H + his \rightleftarrows [H_2(his)]$	20.63	17.48 (8)	10.6 (4)
$3H + his \rightleftarrows [H_3(his)]$	23.1	18.2 (2)	16.4 (7)
$H + hm \rightleftarrows [H(hm)]$	13.36	12.15 (8)	4.1 (4)
$2H + hm \rightleftarrows [H_2(hm)]$	21.64	19.67 (11)	6.6 (5)
$Cu + his \rightleftarrows [Cu(his)]$	13.85	10.6 (1)	10.9 (4)
$Cu + his + H \rightleftarrows [Cu(his)H]$	19.33	13.8 (2)	18.5 (7)
$Cu + 2his \rightleftarrows [Cu(his)_2]$	24.73	19.6 (2)	17.2 (7)
$Cu + 2his + H \rightleftarrows [Cu(his)_2H]$	32.6	25.4 (3)	24 (1)
$Cu + 2his + 2H \rightleftarrows [Cu(his)_2H_2]$	37.0	27 (1)	34 (4)
$2Cu + 2his \rightleftarrows [Cu_2(his)_2H_{-2}] + 2H$	10.95	3.6 (9)	25 (4)
$Cu + 2his \rightleftarrows [Cu(his)_2H_{-1}] + H$	9.28	9 (1)	1 (4)
$Cu + hm \rightleftarrows [Cu(hm)]$	13.04	12.1 (1)	3.2 (4)
$Cu + hm + H \rightleftarrows [Cu(hm)H]$	17.53	17.9 (3)	−1 (2)
$Cu + 2hm \rightleftarrows [Cu(hm)_2]$	21.98	22.2 (2)	−0.7 (7)
$Cu + 2hm + H \rightleftarrows [Cu(hm)_2H]$	29.8	29.0 (3)	3 (2)
$2Cu + 2hm \rightleftarrows [Cu_2(hm)_2H_{-2}] + 2H$	10.15	8.8 (5)	4 (2)
$Cu + 2nm \rightleftarrows [Cu(hm)_2H_{-1}] + H$	7.34	9.8 (6)	−8 (3)
$Zn + his \rightleftarrows [Zn(his)]$	8.91	4.83 (7)	13.7 (3)
$Zn + his + H \rightleftarrows [Zn(his)H]$	15.77	11.4 (3)	15 (2)
$Zn + 2his \rightleftarrows [Zn(his)_2]$	16.26	10.9 (3)	18 (2)
$Zn + hm \rightleftarrows [Zn(hm)]$	7.13	5.72 (8)	4.7 (3)
$Zn + hm + H \rightleftarrows [Zn(hm)H]$	15.61	14.5 (3)	4 (2)
$Zn + 2hm \rightleftarrows [Zn(hm)_2]$	13.89	14.4 (3)	−2 (2)

[a] $\Delta G°$ and $\Delta H°$ in kcal mol^{-1}; $\Delta S°$ in cal mol^{-1} deg^{-1} (1 cal = 4.184 J). [b] References 27-29. [c] Reference 17. [d] 3σ in parentheses.

Let $p_{j'i}\beta_j$ and $1/c_H$ be Y and X, respectively; then by plotting Y vs. X, using a suitable $1/c_H$ range and provided the parameters related to the other species $S_{(j\neq j')}$ are known, one can obtain useful indications as to the existence of the $S_{j'}$ species. In fact, for instance, if for different values of $1/c_H$ and different concentrations $S_{j'}$ is the only species present within the chosen pH range, Y will be a constant. If this is not the case, i.e., if there is a deviation from a straight line, the hypothesis on the species present is not correct in the pH range taken into consideration.

In our case we started off by assuming that only the species [MM′(L)] was present in the first buffered region. But, following the graphical procedure outlined above, we were not able to obtain a constant value for β_{1110}, neither for histidine nor for histamine. Then we supposed that the complex [MM′(L)$_2$] was formed in solution and calculated the value of the function Y for each point of the alkalimetric titration. The Y values plotted vs. $1/c_H$ are consistent with the existence of the hypothesized species.

No other species could be detected for histamine within the range of pH 3–6, whereas, for histidine, the decreasing trend of the curve at lower pH values (Figure 1) strongly points to the presence of a protonated species too, probably of the type [MM′(L)$_2$H]. Similar plots have also been obtained for the other ternary systems. The indications obtained by this graphical method were then confirmed by means of two least-squares programs, namely, MINIQUAD 76A[21] that minimizes the error squares sum in the analytical concentration and a program[20,22] that minimizes the error squares sum in the Z function, where

$$Z = \frac{C_H - C_{OH} - c_H + c_{OH}}{C_M}$$

Furthermore Hamilton's[23] statistical test on the R factor was widely used for all the systems either to prove or to disprove the existence of heterobinuclear complexes and to determine the best set of constants.[24]

In the neutral buffer region of the titration curves, there is a displacement of hydrogen ions exceeding the dissociation of the protonated imidazole and of the amino groups. Both the graphical treatment and the refinement by the two least-squares methods show the presence of a [MM′(L)$_2$H$_{-1}$] species. The precipitation occurring with histamine between pH 7.5 and 8.0 prevents the formation of [MM′(L)$_2$H$_{-2}$] that was found to exist in the histidine systems. By assumption of the existence of the above species the alkalimetric titration curves can be computed with a mean error in c_{OH} values less than ±0.5% for all the ternary systems.

Calculations relative to the purity of the ligands, the refinement of the protonation constants, the $E°$ determination, and the standardization of the stock solution were performed by means of the least-squares computer program ACBA.[25] The enthalpies of complexation were computed by means of the program DOEC.[26]

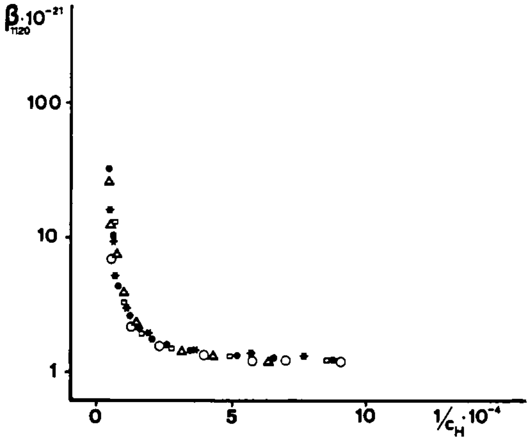

Figure 1. Values of Y vs. c_H^{-1} for the determination of heterobinuclear species relative to the Cu^{II}–Zn^{II}–his$^-$ system: (●) $C_{Cu} = 3$, $C_{Zn} = 6$, $C_{his} = 4.44$; (*) $C_{Cu} = 2.5$, $C_{Zn} = 5$, $C_{his} = 3.5$; (○) $C_{Cu} = 3.5$, $C_{Zn} = 7$, $C_{his} = 4.89$; (□) $C_{Cu} = 4$, $C_{Zn} = 8$, $C_{his} = 6.12$; (△) $C_{Cu} = 3$, $C_{Zn} = 7$, $C_{his} = 5$. (The concentrations are expressed in mmol dm^{-3}.)

The thermodynamic data for the ligand protonation and for the binary complexes of Cu^{II} and Zn^{II} with histamine and L-histidine have already been reported[17] and are summarized in Table III. The copper(II) binary systems were already investigated[27-29] at similar metal to ligand ratios as the ternary complexes reported here. The values of stability constants of dimeric homonuclear species are listed in Table III. In order to ascertain whether the other metal(II) binary systems behave in the same way as copper(II), we performed alkalimetric titrations in which the metal to ligand ratios ranged from 1:4 ($2.5 < C_M < 4$ mmol dm^{-3}) to 3:1 ($C_M \leq 15$ mmol dm^{-3}).

Metal hydroxo species were also considered.[30,31]

Results and Discussion

Simple Complexes. $\Delta G°$, $\Delta H°$, and $\Delta S°$ values relative to the formation of the simple complexes of Ni^{II} and Cd^{II} with L-histidine and Cd^{II} with histamine are listed in Table IV. The thermodynamic data available from the literature[33] for the Ni^{II} complexation are in agreement with our results provided that allowance is made for the different experimental conditions under which they were obtained. The stability constant for

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Table IV. Thermodynamic Values[a] for Simple Complexes of Ni^{II} with L-Histidine and of Cd^{II} with L-Histidine and Histamine at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3)

reaction	log β (3σ)	$-\Delta G°$ (3σ)	$-\Delta H°$ (3σ)	$\Delta S°$ (3σ)
$Ni^{2+} + his^- \rightleftarrows [Ni(his)]^+$	8.67 (3)	11.82 (4)	8.00 (15)	12.8 (6)
$Ni^{2+} + 2his^- \rightleftarrows [Ni(his)_2]$	15.52 (5)	21.15 (7)	16.78 (18)	14.7 (7)
$Cd^{2+} + his^- \rightleftarrows [Cd(his)]^+$	5.74[b]	7.82[b]	4.79 (8)	10.2 (4)
$Cd^{2+} + 2his^- \rightleftarrows [Cd(his)_2]$	9.96[b]	13.58[b]	9.85 (13)	12.5 (5)
$Cd^{2+} + his^- + H^+ \rightleftarrows [Cd(his)H]^{2+}$	11.17[b]	15.22[b]	13.5 (6)	6 (2)
$Cd^{2+} + hm \rightleftarrows [Cd(hm)]^{2+}$	4.76 (3)	6.49 (4)	6.40 (10)	0 (1)
$Cd^{2+} + 2hm \rightleftarrows [Cd(hm)_2]^{2+}$	7.91 (5)	10.78 (7)	12.25 (20)	−5 (1)
$Cd^{2+} + 3hm \rightleftarrows [Cd(hm)_3]^{2+}$	9.93 (6)	13.53 (8)	12.1 (9)	4.7 (2)
$Cd^{2+} + hm + H^+ \rightleftarrows [Cd(hm)H]^{3+}$	11.53 (7)	15.72 (9)	16.9 (3)	−4 (1)

[a] $\Delta G°$ and $\Delta H°$ in kcal mol^{-1}, $\Delta S°$ in cal mol^{-1} deg^{-1}. [b] Reference 32.

Table V. Values of log β for Heterobinuclear Complexes of L-Histidine[a] and Histamine at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3)

reaction	log β
$Cu^{2+} + Ni^{2+} + 2his^- \rightleftarrows [CuNi(his)_2]^{2+}$	21.20
$Cu^{2+} + Zn^{2+} + 2his^- \rightleftarrows [CuZn(his)_2]^{2+}$	20.78
$Cu^{2+} + Cd^{2+} + 2his^- \rightleftarrows [CuCd(his)_2]^{2+}$	20.73
$Cu^{2+} + Ni^{2+} + H^+ + 2his^- \rightleftarrows [CuNi(his)_2H]^{3+}$	25.56
$Cu^{2+} + Zn^{2+} + H^+ + 2his^- \rightleftarrows [CuZn(his)_2H]^{3+}$	25.69
$Cu^{2+} + Cd^{2+} + H^+ + 2his^- \rightleftarrows [CuCd(his)_2H]^{3+}$	25.45
$Cu^{2+} + Ni^{2+} + 2his^- \rightleftarrows [CuNi(his)_2H_{-1}]^+ + H^+$	14.00
$Cu^{2+} + Zn^{2+} + 2his^- \rightleftarrows [CuZn(his)_2H_{-1}]^+ + H^+$	13.02
$Cu^{2+} + Cd^{2+} + 2his^- \rightleftarrows [CuCd(his)_2H_{-1}]^+ + H^+$	12.65
$Cu^{2+} + Ni^{2+} + 2his^- \rightleftarrows [CuNi(his)_2H_{-2}]^0 + 2H^+$	5.45
$Cu^{2+} + Zn^{2+} + 2his^- \rightleftarrows [CuZn(his)_2H_{-2}]^0 + 2H^+$	5.48
$Cu^{2+} + Cd^{2+} + 2his^- \rightleftarrows [CuCd(his)_2H_{-2}]^0 + 2H^+$	<3.9
$Cu^{2+} + Zn^{2+} + 2hm \rightleftarrows [CuZn(hm)_2]^{4+}$	18.00
$Cu^{2+} + Cd^{2+} + 2hm \rightleftarrows [CuCd(hm)_2]^{4+}$	18.36
$Cu^{2+} + Zn^{2+} + 2hm \rightleftarrows [CuZn(hm)_2H_{-1}]^{3+} + H^+$	10.6
$Cu^{2+} + Cd^{2+} + 2hm \rightleftarrows [CuCd(hm)_2H_{-1}]^{3+} + H^+$	10.64

[a] Reference 2.

the equilibrium $Cd^{2+} + 3hm \rightleftarrows [Cd(hm)_3]^{2+}$ is determined in this work for the first time; the formation constant values of mono and bis complexes agree with the literature ones.[34,35] The complexes of the metal ions with L-histidine here reported are enthalpically and entropically favored as were the analogous copper(II) and zinc(II) compounds previously studied (Table III). Cadmium(II) complexes with histamine are only enthalpically stabilized, unlike analogous zinc(II) complexes that are also entropically favored (see Table III). The tendency of the latter ion, which exists as $Zn(H_2O)_6^{2+}$ in aqueous solution,[36] to tetracoordination with tetrahedral geometry can account for the above difference. In fact, in consequence of the decrease of the coordination number there is a release of a number of solvent molecules greater than that of $Cd(H_2O)_6^{2+}$,[37] which tends to form six-coordinated complex species.

The enthalpic changes concerning the formation of mono as well as bis complexes of nickel(II) ion with L-histidine are more exothermic than those of the relative cadmium(II) species. The greater stability of Ni^{II} complexes is ascribable to their larger enthalpic contribution, since no significant $\Delta S°$ differences can be observed.

Both $[Ni(his)_2]$ and $[Cd(his)_2]$ show a positive entropic contribution smaller than that observed in the first step. This marked difference between $\Delta S°_2$ and $\Delta S°_1$ values can be explained considering that the formation of the mono complexes involves a desolvation of the cation greater than that of the bis complexes; thus the number of the solvent molecules released from the first coordination sphere of the metal ion is larger than the number of donor atoms that coordinate in the first complexation step. This interpretation can also account for $\Delta H°_2$ values, which are slightly more exothermic than $\Delta H°_1$ values. By comparing $\Delta H°$ and $\Delta S°$ values of L-histidine complexes with those obtained for the histamine complexes, we can affirm that all potential donor atoms are engaged in the coordination sphere of the metal ions. The histamine complexes are less stable than those with histidine (Table IV), although the enthalpy change is more favorable for the former ones. The lack of histamine of the carboxylic group, which has an endothermic complexation value, can account for what is said above as well as for the unfavorable entropic contribution, due to the nonneutralization of the metal ion charge. The terdentate coordination of L-histidine to nickel(II) and cadmium(II), leading to the formation of six-coordinated bis complexes, is supported by studies on the crystal and molecular structure $[Ni(his)_2]\cdot H_2O$ and $[Cd(his)_2]\cdot 2H_2O$,[38,39] although it should be borne in mind that solution and solid-state structures must be carefully correlated. The tendency of Cd^{II} to form six-coordinated species is also shown by the formation of $[Cd(hm)_3]^{2+}$. No $[Zn(hm)_3]^{2+}$ species was found for zinc(II) ion; this is agreement with our previous assertion about the inclination of Zn^{II} to tetracoordination.

The protonated species $[Cd(his)H]^{2+}$ and $[Cd(hm)H]^{3+}$ show different enthalpic and entropic changes, following a similar trend with respect to that observed in the mono complexes (Table IV). Considering the formation constants of such species as well as the pH range in which they exist, a protonation onto the imidazole nitrogen can reasonably be hypothesized; in the literature the location of the proton in $[M(hm)H]^+$ is still controversial for the analogous complexes of other metal ions.[40]

Mixed-Metal Complexes. In the pH range explored and with the concentration range used (see Table I) we were able to show the existence of two heterobinuclear species, $[MM'(hm)_2]^{4+}$ and $[MM'(hm)_2H_{-1}]^{3+}$, where M = Cu^{II} and M′ = Zn^{II} or Cd^{II}. The former species is already formed in slightly acidic regions, whereas the latter is formed at pH >7. Unlike what was observed for L-histidine complexes, for histamine there is no clear evidence suggesting the existence of protonated species in acidic regions, nor were we able to find complexes such as $[M_2(L)_2]$ below pH 7 (L = his^- of hm and M = Cu^{II}, Ni^{II}, Zn^{II} of Cd^{II}). The formation constants of the ternary species are reported in Table V. Like the L-histidine systems, also the histamine complexes show comparable values of stability constants.

Calorimetric measurements enabled us to determine the thermodynamic parameters of some species only. Problems inherent in the solubility of the complexes as well as the

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Table VI. Thermodynamic Values[a] for Heteronuclear Complexes of L-Histidine and Histamine at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3)

reaction	$-\Delta G°$ (3σ)	$-\Delta H°$ (3σ)	$\Delta S°$ (3σ)
$Cu^{2+} + Zn^{2+} + 2hm \rightleftarrows [CuZn(hm)_2]^{4+}$	24.53 (11)	20.2 (3)	15 (1)
$Cu^{2+} + Cd^{2+} + 2hm \rightleftarrows [CuCd(hm)_2]^{4+}$	25.03 (7)	21.21 (3)	12 (2)
$Cu^{2+} + Ni^{2+} + 2his^- \rightleftarrows [CuNi(his)_2]^{2+}$	28.90 (5)	21.4 (5)	25 (2)
$Cu^{2+} + Zn^{2+} + 2his^- \rightleftarrows [CuZn(his)_2]^{2+}$	28.32 (5)	18.8 (5)	32 (2)
$Cu^{2+} + Cd^{2+} + 2his^- \rightleftarrows [CuCd(his)_2]^{2+}$	28.25 (5)	19.5 (4)	29 (2)
$Cu^{2+} + Zn^{2+} + 2his^- + H^+ \rightleftarrows [CuZn(his)_2H]^{3+}$	35.0 (1)	25.4 (5)	32 (3)
$Cu^{2+} + Cd^{2+} + 2his^- + H^+ \rightleftarrows [CuCd(his)_2H]^{3+}$	34.7 (1)	27.3 (5)	25 (3)

[a] $\Delta G°$ and $\Delta H°$ in kcal mol^{-1}; $\Delta S°$ in cal mol^{-1} deg^{-1}.

Table VII. Thermodynamic Values, Construed from the Literature Data, Accompanying the Different Type of Coordination Hypothesized for the Heteronuclear Complexes of L-Histidine with Copper(II) and Zinc(II) Ions

reaction[a]	$-\Delta H°$, kcal mol^{-1}		$\Delta S°$, cal mol^{-1} deg^{-1}	
$Zn^{2+} + 2hm \rightleftarrows [Zn(hm)_2]^{2+}$ [b]	−10.41	8.4	11.6	22.3
$Cu^{2+} + 2ac^- \rightleftarrows [Cu(ac)_2]$ [c]	2.0		10.7	
$Zn^{2+} + 2gly^- \rightleftarrows [Zn(gly)_2]$ [d]	−6.3	18.9	22.1	15.1
$Cu^{2+} + 2im \rightleftarrows [Cu(im)_2]^{2+}$ [e]	−12.6		−7.0	
$Zn^{2+} + 2ac^- \rightleftarrows [Zn(ac)_2]$ [f]	5.26	17.0	23.7	22.8
$Cu^{2+} + 2hm \rightleftarrows [Cu(hm)_2]^{2+}$ [b]	−22.24		−0.9	
$Zn^{2+} + hm + gly^- \rightleftarrows [Zn(hm)(gly)]^+$ [g]	(−2.76) + (−5.72)	14.4	(15.4) + (4.7)	25.9
$Cu^{2+} + im + ac^- \rightleftarrows [Cu(im)(ac)]^+$	(−7.2) + (1.24)		(−4.2) + (10)	
$Zn^{2+} + im + ac^- \rightleftarrows [Zn(im)(ac)]^+$ [h]	(−4.0) + (2.04)	19.8	(−3.0) + (11.2)	28.6
$Cu^{2+} + hm + gly^- \rightleftarrows [Cu(hm)(gly)]^+$ [i]	(−12.02) + (−5.87)		(3.4) + (17)	
$Zn^{2+} + 2im \rightleftarrows [Zn(im)_2]^{2+}$ [h]	−8	21.5	−6	17
$Cu^{2+} + 2gly^- \rightleftarrows [Cu(gly)_2]$ [i]	−13.5		23	

[a] im = imidazole, ac^- = acetate ion, gly^- = glycinate ion. [b] Reference 17. [c] Reference 42. [d] Reference 43. [e] Reference 44. [f] Reference 45. [g] Reference 46. [h] Reference 47. [i] Reference 48.

sensitivity of the experimental apparatus prevented the determination for both L-histidine and histamine of the complexation heats of the species formed in the alkaline region. The thermodynamic parameters relative to the formation of ternary complexes (Table VI) show negative enthalpic and positive entropic contributions. If compared with L-histidine, histamine complexes are enthalpically more favored whereas entropically less favored. This trend is similar to that of the binary mono complexes (see Tables III and IV). Thus, on the basis of the previous interpretation given for the simple complexes, it can be asserted that, also in these mixed complexes, all potential donor atoms are involved in bonding to the metal ions. $[CuCd(hm)_2]^{4+}$ is slightly more stable than $[CuZn(hm)_2]^{4+}$; this can be ascribed to a higher enthalpic contribution. This difference in $\Delta H°$ values is slightly more marked for the histamine complexes than for the analogous species with L-histidine, but it is still of the same order of magnitude as the parent binary complexes (see Tables III and IV). This, in addition to copper(II) coordinating to nitrogen atoms, seems to indicate also a nonnegligible interaction between histamine donor atoms and cadmium(II) or zinc(II). The larger enthalpic change of Cd^{II} heteronuclear complexes with respect to the analogous Zn^{II} species can probably be correlated to the larger size of Cd^{II}.

Considering the formation $\Delta S°$ of simple complexes and the "stiffening" of the ligand around the two metal ions, the $\Delta S°$ change accompanying the formation of the ternary complexes is, at first sight, rather surprising, owing to its significantly positive values. This datum induces us to exclude, for these complexes, a planar structure analogous to that found for the Cu^{II} bis complex with histamine.[41,17] The entropic parameters, instead, seem to indicate the presence in these heterocomplexes of a tetrahedral distortion with a probable bulk effect of the ligand coordinated to the two metal ions. In this respect what is significant is the larger entropic contribution of the zinc(II) with respect to the cadmium(II) complex, consequent to the preference of the former to be tetrahedrally coordinated. The mixed-metal complexes of L-histidine show comparable $\Delta G°$ but quite different $\Delta H°$ and $\Delta S°$ values (Table VI). The ternary complex $[CuNi(his)_2]^{2+}$ is enthalpically more favored than those containing Cd^{II} or Zn^{II}, which, on the contrary, show a larger entropic stabilization.

By comparing the formation thermodynamic parameters of histidine ternary complexes with the histamine ones, it has been possible to affirm that all potential donor atoms were bound to the metal ions. A comparison between mixed systems, formed by two ligands, is not so useful for defining the arrangement of L-histidine around the different pairs of cations. In order to form an idea of the type of coordination, we took into consideration several hypotheses on the disposition of the donor atoms coordinated to the metal ions by calculating the values of the thermodynamic parameters on the basis of data available in the literature.

From our hypothesis, coordinations thermodynamically less favored, as for instance those implying the formation of seven-membered chelate rings, were excluded (histidine chelating through the imidazole nitrogen and the carboxylic oxygen). From the values obtained (Table VII) a histamine-like coordination of Zn^{II} in the complex $[CuZn(his)_2]^{2+}$ has to be excluded, owing to the small $\Delta H°$ that would accompany the complexation value which, instead, has been found to be rather high. For the same reason a histamine- and glycine-like coordination of Zn^{II} has to be excluded. Only glycine-like coordination of the metal ion has to be rejected, because of the excessively small $\Delta S°$ value which would result. Among the other three coordinations supposed to be likely, we are inclined to that where zinc(II) ion is bound to the imidazole nitrogen

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of a histidine molecule and to the carboxylic group of the other histidine molecule. Simultaneously Cu^{II} would be bound glycine-like to a ligand molecule and histamine-like to the other. This not only because the thermodynamic parameter values obtained (Table VII) are, on the whole, the most close to the experimental ones (Table V) but also because the hypothesis accounts for the enthalpic and entropic trend of the heteronuclear complexes $[CuNi(his)_2]^{2+}$, $[CuZn(his)_2]^{2+}$, and $[CuCd(his)_2]^{2+}$. In fact, with examination the other two possible hypotheses (Zn^{II} coordinates to two carboxylic oxygens or to two imidazole nitrogens of two different L-histidine molecules) the difference between the formation $\Delta H°$ of the two species $[CuZn(his)_2]^{2+}$ and $[CuCd(his)_2]^{2+}$ should clearly be higher than that found, owing to the more "soft" character of Cd^{II} compared with Zn^{II}.

The positive and fairly large entropic contribution, consequent to the formation of these binuclear complexes, in spite of the "stiffening" of the ligand coordinated to two different metal ions, can be accounted for by hypothesizing a "secondary" interaction between Ni^{II}, Zn^{II}, or Cd^{II} with the neighboring donor atoms "primarily" bound to Cu^{II}. This interaction would encourage Cd^{II} and Zn^{II} more than Ni^{II} desolvation, following a trend that can be related to the different tendency to six-coordination of the above metal ions (Ni > Cd > Zn and $\Delta S°$ = 25, 29, and 32 eu).

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Registry No. L-Histidine, 71-00-1; histamine, 51-45-6; Cu, 7440-50-8; Ni, 7440-02-0; Zn, 7440-66-6; Cd, 7440-43-9.

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Copper Halide Containing Photochromic Glasses

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The melting and characterization of photochromic alkali aluminoborosilicate glasses containing copper halide are reported. The glasses have high initial transmittance (72–86%) and can darken to 14% under simulated solar irradiation. The darkened glass absorption spectrum is broad, maximizing at 580 nm. A process for darkening is proposed in which copper colloids are formed. Photochromism is demonstrated in glasses of 44–51 cation % silica. At any given silica and alumina level, a certain alkali to boric acid ratio is necessary to achieve photochromism. This ratio decreases as silica and alumina increase.

Photochromic glasses containing a number of different crystallites in suspension have been reported.[1] Metal halides[2] and silver halides[3] in particular have received considerable attention. Silver halide containing glasses have found application in ophthalmic ware and have been proposed for use in automotive and architectural glazing.

The photochromic characteristics of silver halide containing glasses vary considerably with glass composition, but certain properties are common to all the glasses. Glasses containing silver halide darken in response to UV or longer wavelength visible light. Thermal and optical fading rates are sensitive to both base glass composition and "photochromic element" addition (silver, halogen, and copper). Silver halide containing glasses show varying degrees of temperature dependence of the steady-state darkening level and are subject to a maximum temperature limit above which no darkening will be observed.

Several photosensitive copper compounds have been reported. Darkening upon irradiation has been observed for CuCl(s) and CuBr(s) in suspension in aqueous solution and in gelatine.[4] $CuC_2O_4 \cdot {}^1/_2H_2O$ has been examined[5] as a potential high-speed photographic material. In these cited studies and in the work of Roginskii et al.[6] on the same compounds, the principle products of photolysis are Cu and Cu_2O. A photochromic reverse reaction is not noted in any of these studies. Tsekhomskii[7] has reported a CuCl-containing glass which shows photochromic darkening and fading, although crystallite size is estimated at considerably greater than 100 Å causing reduced transmittance due to scattering before photochromic darkening.

The characterization of a range of copper halide containing photochromic glasses which show high initial transmittance and photochromic response similar to silver halide containing glasses is now communicated. Base glasses have been examined in a mixed-alkali aluminoborosilicate system, with variation in the photochromic elements Cu, Cl, Br, and F. Photochromic properties of the glasses have been examined from the standpoint of pertinent parameters such as darkening level, spectral response, thermal bleaching rate, temperature dependence of darkening, and induced absorption spectrum. The examination of these data allows speculation on the photochromic mechanism in copper halide photochromic glasses.

Experimental Section

All glasses were batched with use of reagent grade batch materials and melted in covered 500-cm³ platinum crucibles. Glass was melted in Glo-bar furnaces at 1400 °C and stirred before being poured into slabs and annealed at 375–450 °C overnight. After annealing, samples of the glasses were subjected to heat treatment to develop photochromism, typically at a temperature between 580 and 680 °C for 10–60 min. All operations were performed in air. Some atmospheric control of redox conditions is possible, but compositional control is

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