Ternary Copper(II) Complexes with 2,2′-Bipyridine and *N*-Tosyl-substituted Amino Acids. Part 1. Polarographic and pH-Metric Study†

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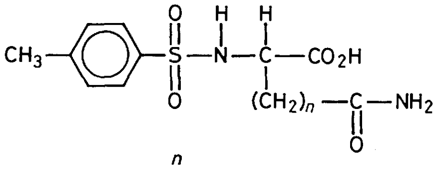
The solution behaviour of ternary complexes of Cu^{2+} with 2,2′-bipyridine (bipy) and *N*-tosyl (toluene-4-sulphonyl) derivatives of asparagine and glutamine was investigated by pH-metric and polarographic tools, and compared with the corresponding binary Cu^{2+}–*N*-tosylamino acidate systems. The experimental techniques agree about the type and stability of the complex species, in which the amino acidic ligands co-ordinate through the carboxylate group (HL^-) or act as bidentate ligands through the carboxylic oxygen and the deprotonated sulphonamide nitrogen (L^{2-}) [HL^- and L^{2-} = *N*-tosyl-DL-asparaginate (or -L-glutaminate) monoanion and dianion respectively]. The following prevailing species were detected: [Cu(bipy)$(HL)_2$], [Cu(bipy)L], and [Cu(bipy)L_2]$^{2-}$. Evidence has also been obtained for the presence of the species [Cu(bipy)(HL)]$^+$ and [Cu_2(bipy)$_2L_2$(OH)]$^-$. The copper(II)-promoted sulphonamide deprotonation of the amino acidic ligands in the ternary systems is observed at lower pH values than that in the corresponding binary systems (pH ≈ 5 *vs.* pH ≈ 7); this effect was not observed for the peptide-nitrogen deprotonation of the ternary copper(II) complexes of peptides with 2,2′-bipyridine.

The *N*-tosyl derivatives of asparagine and glutamine co-ordinate the copper(II) ion in a pH-dependent fashion, by acting as simple carboxylates below pH 5 and as bidentate ligands through the carboxylate oxygen and the deprotonated sulphonamide nitrogen at higher pH.[1] The species found to prevail in the above pH ranges were [Cu$(HL)_2$] and [CuL_n]$^{(2n-2)-}$, respectively [HL^- and L^{2-} = *N*-tosyl-DL-asparaginate (or-L-glutaminate) monoanion and dianion respectively].[1] This co-ordinative behaviour, characteristic of amino acids *N*-protected by an aryl-sulphonic group,[2,3] parallels in some way that observed for oligopeptides interacting with several metal ions:[4] both types of ligands undergo metal-promoted amide-nitrogen deprotonation, and the various metal ions show a conserved order of efficiency. In this paper we report an investigation of the solution behaviour of the ternary copper(II) systems given by *N*-tosyl-DL-asparagine (tsasn) and -L-glutamine (tsgln) with 2,2′-bipyridine (bipy) with the aim to determine how the aromatic base influences the pH-dependency of the ligand binding mode, since in the corresponding ternary copper(II) complexes given by oligopeptides, 2,2′-bipyridine was found to disfavour the substitution of the metal ion for the peptide nitrogen-bound hydrogen, thus increasing the pK_{NH} values from 4—5, observed for the binary systems, to about 8.[4,5] The present systems have been investigated by potentiometry and polarography, and characterized in terms of complex species prevailing in different pH ranges and ligand-to-metal ratios. In the following paper (Part 2), the influence of 2,2′-bipyridine on the ligand co-ordination behaviour in the solid state will be discussed.

Experimental

The ligands tsasn and tsgln were recrystallized from a 1:1 ethanol–water solution and the concentration of the solutions used throughout was tested potentiometrically. Copper(II) perchlorate hexahydrate was from Fluka and the concentration of the stock solution was determined with ethylenediaminetetra-acetic acid. Solutions of 2,2′-bipyridine (C. Erba) were standardized potentiometrically with strong acid.



	n
tsasn	1
tsgln	2

Polarography.—The investigation of the Cu^{2+}–*N*-tosylaminoacidate binary systems was carried out on aqueous solutions containing a constant Cu^{2+} concentration of 5×10^{-4} mol dm^{-3} with ligand-to-metal ratios varying from 2:1 to 20:1. In the study of the ternary systems the same Cu^{2+} concentration was used with Cu^{2+}:bipy:H_2L ratios of 1:1:2, 1:1:4, 1:1:6, 1:1:8, 1:1:10, and 1:1:20. The pH of the solutions was varied by adding aqueous NaOH (32%). $NaClO_4$ was used as base electrolyte and the ionic strength kept constant (I = 0.1 mol dm^{-3}). The pH measurements were performed with an Amel-337 pH-meter using an Ingold HA 405-60-K1 pH-combined electrode. Polarographic measurements were carried out with an Amel Multipolarograph 472 at 25 ± 0.1 °C; a saturated calomel electrode (s.c.e.) was used as reference, and all $E_{\frac{1}{2}}$ values are referred to s.c.e. The accuracy of the $E_{\frac{1}{2}}$ value is ±0.005 V. The reduction processes were examined by changing the Cu^{2+} ion concentration from 1×10^{-4} to 5×10^{-4} mol dm^{-3} (with the above Cu^{2+}:H_2L and Cu^{2+}:bipy:H_2L ratios) and by using dropping times of 1,2,3, and

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† *Supplementary data available* (No. SUP 56764, 7 pp.): other polarographic and pH-metric data, species distribution curves. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

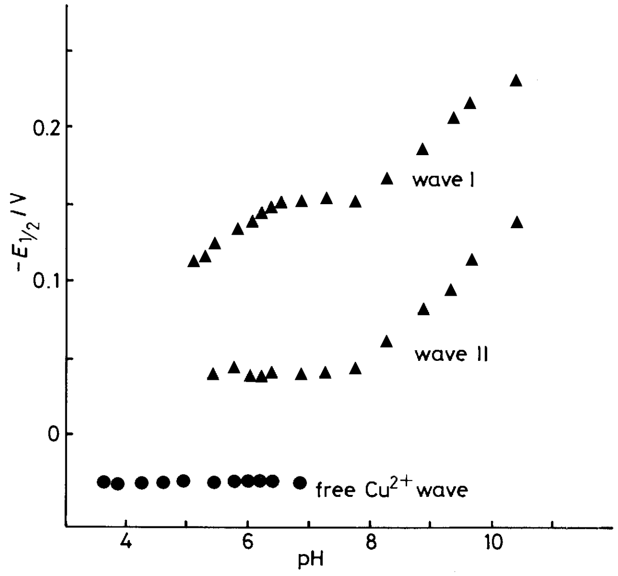

Figure 1. Plot of $-E_{\frac{1}{2}}$ *vs.* pH for the Cu^{2+}–tsasn system. Concentrations (mol dm^{-3}): Cu^{2+}, 5×10^{-4}; tsasn, 1×10^{-3} (for the sake of clarity, only one ligand concentration is reported); $T = 25$ °C; dropping time = 1 s

4 s. The reversibility of the processes was determined from the semilogarithmic analysis of the polarographic waves and checked by voltammetric measurements at 100 mV s^{-1}. The dependence of the limiting current values on the dropping time and the depolarizer concentration shows the diffusive nature of the processes. The number of electrons involved in the reduction of the complexes was determined by means of the Ilkovic equation,[6] and for the reversible processes was confirmed by the difference between the potential of the cathodic and anodic peak in cyclic voltammetry.

Potentiometry.—Potentiometric measurements were performed at 25 ± 0.1 °C with the fully automatic Orion 960 Autochemistry system[7] using a Ross 8102 SC combined electrode and a Centronic GLP II printer for recording e.m.f. measurements, pH readings, and titration curves. Sodium hydroxide (carbonate-free) (C. Erba) standardized against phthalate (N.B.S.) was used as a titrant. The standard electrode potential E^0 was determined before and after each experiment by titration of a known amount of $HClO_4$ (0.1 mol dm^{-3}) with a standard NaOH solution. The ionic product K_w was calculated in the alkaline region of each calibration curve. The liquid-junction potentials were found reproducible and rather small as compared to the potential of the cell (about 2%), consequently they were neglected in the calculations. All experiments were carried out under a nitrogen atmosphere, determining the equivalent point by the first derivative technique[7] with constant cm^3 or mV increments in order to obtain at least 25 experimental points for each titration. The starting solutions for each titration were prepared by adding successively to the titration vessel known volumes of $Cu(ClO_4)_2$, bipy, and amino acidic ligand solutions in order to obtain 1:1:2 and 1:1:4 molar ratios. The amino acidic ligand concentration varied from 2.7×10^{-3} to 5.5×10^{-3} and from 3.8×10^{-3} to 4.5×10^{-3} mol dm^{-3} for tsgln and tsasn respectively. The ionic strength was adjusted to 0.1 mol dm^{-3} with $NaClO_4$.

The stability constants were obtained by using the SUPERQUAD program[8] and the species distribution curves from the DISPO program.[9] During refinements $\sigma_E = 0.3$ (mV error) and $\sigma_V = 0.005$ (volume error) were employed. All the calculations were performed with an IBM XT 286 personal computer.

Results and Discussion

Cu^{2+}–*N-Tosylaminoacidate Systems.*—The ligands show a quite similar polarographic and pH-metric behaviour, accordingly, only figures for tsasn are reported. (Those relative to tsgln are available in SUP No. 56764, as well as those for the ternary systems.) In the polarographic study (Figure 1) at values up to pH 5.5 only one reversible wave is present: besides being bielectronic and diffusion controlled, its $E_{\frac{1}{2}}$ and i_d values are independent of pH and ligand-to-metal ratio. These features and the $E_{\frac{1}{2}}$ value of 0.03 V indicate that it corresponds to the free Cu^{2+} ion reduction.[10] At higher pH values two new waves (wave I and II) appear at about −0.13 and −0.05 V respectively, again showing a bielectronic, reversible, and diffusion controlled nature. With increasing pH, their i_d values increase to the detriment of that of the former wave which disappears at *ca.* pH 7. At higher pH values the i_d values of both wave I and II do not change until metal hydroxide precipitation occurs. The pH-behaviour of the $E_{\frac{1}{2}}$ values is the same for both waves, but different $E_{\frac{1}{2}}$ dependencies from the ligand concentration are observed. In particular, while the half-wave potential of wave II decreases with increasing ligand concentration, that of wave I is not influenced by the metal-to-ligand ratio. The determination of the species present in solution and their stability constants (Table) was performed as described for the system Cu^{2+}–*N*-tosylglycinate,[2] which showed nearly identical polarographic and spectrophotometric behaviour. In particular, wave II corresponds to the reduction of the species [CuL] and $[CuL(OH)]^-$ below and above pH 8 respectively, while wave I is due to the reduction of the $[Cu(HL)_2]$ and $[CuL_2]^{2-}$ species, and the corresponding mixed-hydroxo complexes. The stability constants were determined by using the Shaap–McMasters method.[11] The same binary species with the same stabilities were revealed by the potentiometric analysis (see the Table).[1]

Cu^{2+}–*bipy*–*N-Tosylaminoacidate Systems.*—In the pH-metric titrations two equivalent points were observed for the system containing tsgln, the first and second corresponding to amounts of NaOH given by equations (1) and (2) respectively

$$m_{NaOH} = m_{tsgln} \qquad (1)$$

$$m_{NaOH} = m_{tsgln} + 1.5\, m_{Cu} \qquad (2)$$

(m = number of moles). For the tsasn system only the second equivalent point is observed. The features of the pH-metric curves, and the behaviour of the Cu–ligand binary systems[1] suggest the existence of the following species, which lead to a good convergence of the fitting process: $[Cu(bipy)(HL)_2]$, [Cu(bipy)L], $[Cu_2(bipy)_2L_2(OH)]^-$, and $[Cu(bipy)L_2]^{2-}$. The stability constants obtained by either considering Cu^{2+} or $[Cu(bipy)]^{2+}$ ($\log \beta^{Cu}_{Cu(bipy)} = 8.0$)[12] as a starting species are in good agreement. The species $[Cu_2(bipy)_2L_2(OH)]^-$ was hypothesized from the equation relative to the second equivalent point. The stability constants and the species distribution curves are reported in the Table and Figure 2 respectively.

The polarographic investigation on the ternary systems was performed with a constant Cu^{2+}:bipy ratio of 1:1. The same qualitative behaviour (Figure 3) was observed for both ligands. For tsasn (tsgln) up to pH 4.5 (5.2) two waves were observed, one of which, with a nearly constant $E_{\frac{1}{2}}$ value of 0.03 V, can be assigned to the Cu^{2+} ion reduction; the other wave, with a negative $E_{\frac{1}{2}}$ value (wave I) is again reversible, bielectronic, and diffusion controlled, and its i_d value increases with increasing

Table. log β of complexes prevailing at different pH[a]

		log β[b]				log β[b]		Δ log K[b]	
Ternary species	pH	*c*	*d*	Binary species	pH	*c*	*d*	*c*	*d*
$[Cu(bipy)(HL)]^+$	3—4		10.1[e] (10.2)[e]						
$[Cu(bipy)(HL)_2]$	3—4	12.5 (12.5)	12.3 (12.4)	$[Cu(HL)_2]$	<4.5	4.4 (4.4)	4.3 (4.4)	0.1 (0.1)	0.1 (0.1)
$[Cu(bipy)L]$	4—5.4	17.5 (17.4)	17.6 (17.5)	$[CuL]$	4.5—7.6	9.3 (9.0)	9.1 (9.0)	0.2 (0.4)	0.6 (0.6)
$[Cu_2(bipy)_2L_2(OH)]^-$	5.4—9.4	41.8 (41.8)	*e* (*e*)						
$[Cu(bipy)L_2]^{2-}$	>9.4	23.8 (23.8)	23.1 (23.2)	$[CuL_2]^{2-}$	>7.6	16.5 (16.0)	16.3 (15.8)	−0.7 (−0.2)	−1.1 (−0.5)

[a] Overall stability constants (β) are relative to the equilibrium: $Cu^{2+} + bipy + nHL\ (or\ L) \rightleftharpoons [Cu(bipy)(HL)_n]$ {or $[Cu(bipy)L_n]$}. [b] Values refer to tsasn species, those in parentheses to tsgln species. [c] Potentiometric value. [d] Polarographic value. [e] See text.

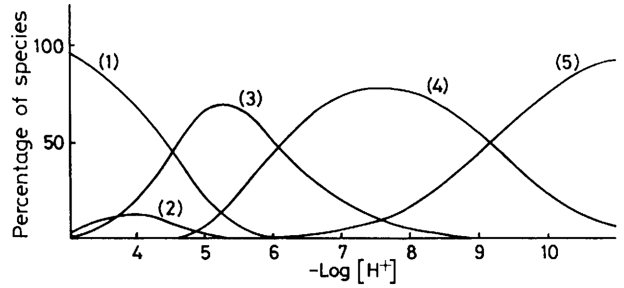

Figure 2. Species distribution curves for the complexes at 4:1:1 ligand–metal–bipy molar ratio; $[Cu(bipy)]^{2+}$ (1), $[Cu(bipy)(HL)_2]$ (2), $[Cu(bipy)L]$ (3), $[Cu_2(bipy)_2L_2(OH)]^-$ (4), $[Cu(bipy)L_2]^{2-}$ (5). Concentrations (mol dm^{-3}): Cu^{2+} and bipy, 1.125×10^{-3}; tsasn, 4.5×10^{-3}

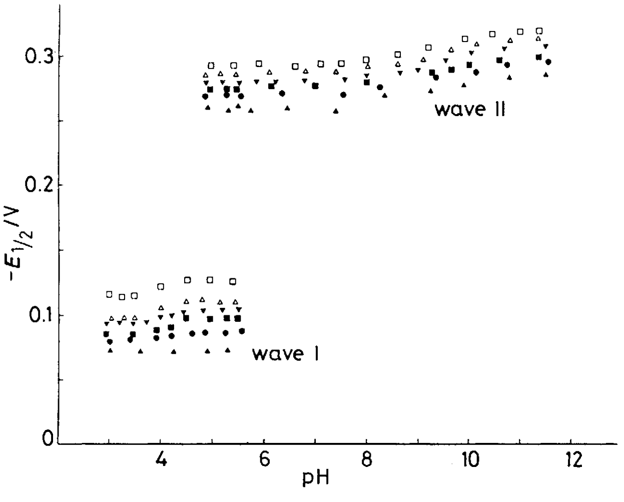

Figure 3. Plot of $-E_{\frac{1}{2}}$ *vs.* pH for the Cu–bipy–tsasn system. Concentrations (mol dm^{-3}): Cu^{2+} and bipy, 5×10^{-4}; tsasn, 1×10^{-3} (▲), 2×10^{-3} (●), 3×10^{-3} (■), 4×10^{-3} (▼), 5×10^{-3} (△), 1×10^{-2} (□); T = 25 °C; dropping time = 1 s

pH and ligand concentration to the detriment of the former wave. In addition, the $E_{\frac{1}{2}}$ value of wave I decreases with increasing ligand concentration and is pH-dependent only up to pH around 4.5. At values higher than pH 4.5 (5.2) a new wave (wave II) appears with $E_{\frac{1}{2}}$ values more negative than wave I and again decreasing with increasing pH and ligand concentration. Besides being bielectronic and diffusion controlled, this wave is found to be irreversible. Its i_d value increases with increasing pH while that of the other waves decreases until they disappear at pH ≈5.5. The sum of the various i_d values is always constant in the pH range investigated. From inspection of the species distribution curves of Figure 2, wave I appears for both ligands in the pH region in which the $[Cu(bipy)]^{2+}$ and $[Cu(bipy)(HL)_n]^{(2-n)+}$ (n = 1 or 2) species prevail, while wave II begins to appear at pH values in which the prevailing species are those produced by the deprotonation of the sulphonamide nitrogen of the ligand tsasn or tsgln. Accordingly, we can confidently assign wave I to reduction processes involving species in which the ligand binds through the carboxylate group, and wave II to those of species in which the ligand acts as bidentate through the carboxylate oxygen and the deprotonated sulphonamide nitrogen.

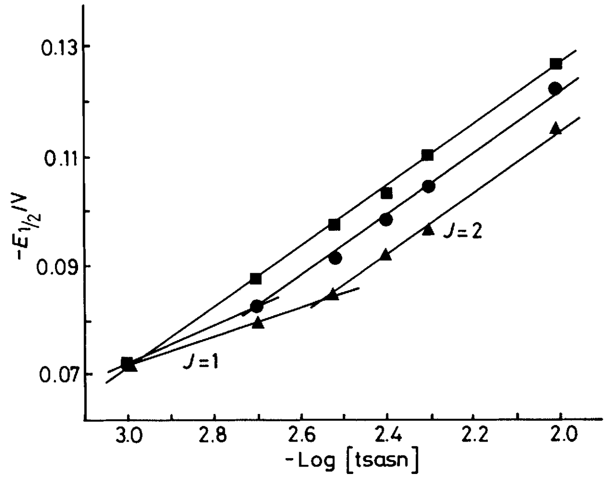

Figure 4. Plot of $-E_{\frac{1}{2}}$ *vs.* −log [tsasn] for the Cu^{2+}–bipy–tsasn system (wave I) at different pH values: 3.5 (▲), 4.0 (●), 4.5 (■)

The reversibility of wave I allows the use of the Lingane method[6] to determine the ligand co-ordination number (J) as either 1 or 2, the latter being favoured with increasing pH and ligand concentration (Figure 4). The Shaap–McMaster method was applied for the determination of the species and their stability constants: the presence of mixed-hydroxo species at pH lower than 12 was ruled out due to the pH-independent behaviour of the $E_{\frac{1}{2}}$ value. Besides the $[Cu(bipy)]^{2+}$ species, the ternary complexes $[Cu(bipy)(HL)_2]$ and $[Cu(bipy)(HL)]^+$ were found to be present, the latter being a minor species (it was not revealed by the potentiometric analysis). Their stability constants (β) are reported in the Table. A $\beta^{Cu}_{Cu(bipy)}$ value of 7.9, quite close to the literature data,[12] was determined. As far as the irreversible wave II is concerned, the stability constants of

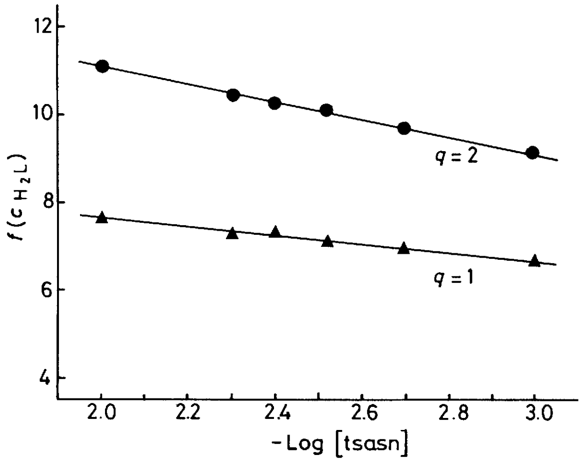

Figure 5. Plot of $f(c)$ *vs.* $-\log$[tsasn] [see equation (4)] for the Cu–bipy–tsasn system (wave II) at different pH values: 5.2 (▲); 10.5 (●)

the various species referred to the equilibrium (3) are given by

$$[\mathrm{Cu(bipy)}]^{2+} + n\,\mathrm{L}^{2-} \rightleftharpoons [\mathrm{Cu(bipy)L}_n]^{(2-2n)+} \quad (3)$$

$$\log\beta + q\log c = \log\left\{\frac{i_\mathrm{d} - i}{i} - \left[\frac{c\,(0, t_1)}{c}\right]^{q-p} \cdot \exp\frac{\alpha nF}{RT}\left[E - (E_{\frac{1}{2}})_\mathrm{irr}\right]\right\} - \frac{nF}{2.3\,RT}\left[E - E_{\frac{1}{2}}^{\mathrm{Cu(bipy)}}\right] = f(c) \quad (4)$$

equation (4). This is derived from the equation given by Elenkova *et al.*,[13] simply by substituting the standard redox potential of the metal E°_M with the reversible $E_{\frac{1}{2}}^{\mathrm{Cu(bipy)}}$ potential (-0.055 V): c is the total ligand concentration, $c(0, t_1)$ is the ligand concentration at the electrode surface at the time t_1, α is the charge transfer coefficient, q is the maximum co-ordination number of the species in the bulk of the solution, and p is that of the species undergoing reduction at the electrode [in general $c = c(0, t_1)$ and $p = q$]. This equation holds for all degrees of irreversibility and ligand-to-metal ratios. The analysis of wave II performed at pH lower than 7 and higher than 9 (conditions in which $E_{\frac{1}{2}}$ is independent of pH) indicates [Cu(bipy)L] and $[\mathrm{Cu(bipy)L_2}]^{2-}$ to be the prevailing species respectively (Figure 5). Their overall stability constants, calculated by using the above $\log\beta^{\mathrm{Cu}}_{\mathrm{Cu(bipy)}}$ value of 7.9, are reported in the Table. In the intermediate range pH 7—9, $E_{\frac{1}{2}}$ depends upon pH, and a titration pattern corresponding to the transformation (5), is clearly observed. Since equation

$$[\mathrm{Cu(bipy)L}] + \mathrm{HL}^- + \mathrm{OH}^- \longrightarrow [\mathrm{Cu(bipy)L_2}]^{2-} + \mathrm{H_2O} \quad (5)$$

(4) cannot be applied when a potential additional ligand (OH^-) is present, we cannot determine if the above addition of a second amino acidic ligand takes place with the involvement of an intermediate species, this possibly being the dimeric $[\mathrm{Cu_2(bipy)_2L_2(OH)}]^-$ species, as indicated by the potentiometric analysis. Nevertheless, equation (4) can indicate the ligand-to-metal ratio of the prevailing species in the above pH range: such a value is found equal to 1, in agreement with the potentiometric result. A reasonable ligand arrangement of the dimeric species is that with bipy in an axial-equatorial position, the bidentate L^{2-} molecule in the metal co-ordination plane, and an equatorial hydroxo ion as a bridging ligand.

An interesting observation resulting from this investigation is the occurrence of the copper-promoted sulphonamide deprotonation in the ternary systems at lower pH values as compared with the binary ones. This effect, qualitatively already observed in a previous investigation on the Cu^{2+}–bipy–*N*–dansylglycinate system,[14] is indicated by the following comparison of ternary and binary systems. The pH-metric titration curves of the ternary systems give apparent pK values of sulphonamide nitrogen deprotonation lower than those observed in the binary systems for tsasn: $\mathrm{p}K^{\mathrm{CuL}}_{\mathrm{NH}} = 7.5 \pm 0.1$, $\mathrm{p}K^{\mathrm{Cu(bipy)L}}_{\mathrm{NH}} = 5.5 \pm 0.1$; for tsgln: $\mathrm{p}K^{\mathrm{CuL}}_{\mathrm{NH}} = 7.5 \pm 0.1$, $\mathrm{p}K^{\mathrm{Cu(bipy)L}}_{\mathrm{NH}} = 5.7 \pm 0.1$]; in the species distribution curves the 'deprotonated' species appear at lower pH values in the ternary systems than in the binary systems;[1] the polarographic wave II in the ternary systems appears at lower pH values than waves I and II in the binary systems. Accordingly, both techniques give positive $\Delta\log K$ values [$\Delta\log K = \log K^{\mathrm{Cu(bipy)}}_{\mathrm{Cu(bipy)L}} - \log K^{\mathrm{Cu}}_{\mathrm{CuL}}$][4a] for the species bearing one deprotonated L^{2-} molecule (Table). In addition, on increasing from pH 3 to 6.5 the visible spectra of the ternary systems show a blue shift (from 650 to 630 mn for tsasn and from 685 to 670 mn for tsgln) consistent with the $\lambda_{\mathrm{max.}}$ decrease on passing from a $\mathrm{CuN_2O}_x$ to a $\mathrm{CuN_3O}_x$ chromophore in the solid state; at higher pH values $\lambda_{\mathrm{max.}}$ remains unchanged. Such a spectral change occurs at lower pH values than that observed in the binary systems relative to the involvement of the deprotonated sulphonamide nitrogen of the first ligand molecule in metal co-ordination (pH 4.5—7.5).

While the positive (though quite small) $\Delta\log K$ values obtained for the $[\mathrm{Cu(bipy)(HL)_2}]$ species are in line with the general behaviour of the carboxylate ligands,[4a] and the negative values for the ternary species containing two deprotonated L^{2-} molecules are straightforwardly due to their sizable steric hindrance, the positive $\Delta\log K$ values for the [Cu(bipy)L] species raise some interest if compared with the generally observed negative values for ternary copper(II) complexes with 2,2′-bipyridine and peptides (indeed in the latter species the amide proton is displaced at higher pH values than in the corresponding binary species).[4a] In the present systems the lowering effect of 2,2′-bipyridine on the $\mathrm{p}K_\mathrm{a}$ of copper-promoted sulphonamide-nitrogen deprotonation and the corresponding higher stability of the ternary [Cu(bipy)L] species as compared with the [CuL] species may be reasonably due to at least two concomitant effects. First, the carboxylate group, which acts as the primary ligating group ('anchoring group'), interacts more strongly with the $[\mathrm{Cu(bipy)}]^{2+}$ species as compared with the Cu^{2+} ion thus favouring in the former case the formation of the chelate ring [the anchoring group of peptides (the terminal amino group) behaves in the opposite way];[4a] in addition, the stability of these 'deprotonated' ternary complexes may be linked, as already proposed for oxygenated ligands,[4a] to a co-operative effect of the π systems of the ligands, the aromatic ring of the ligand being conjugated to the amino acidic moiety through the sulphur atom.[15] This could explain the remarkable stability of the species [Cu(bipy)L] obtained with *N*-dansylglycine, bearing a naphthalene group linked to $\mathrm{SO_2}$, which separates in the solid state at pH 5.5.[14] Positive $\Delta\log K$ values for ternary copper (II) complexes with 2,2′-bipyridine and *N*,*O*-ligands (N neutral) were previously attributed to stacking interactions between 2,2′-bipyridine and the aromatic group of the ligand.[16] Such interactions have not been found in the complexes separated in the solid state (Part 2) as well as in several other *X*-ray investigations of $\mathrm{Cu^{II}}$–bipy–*N*-tosylaminoacidate complexes.[17]

If the above bipy effect is conserved for the *N*-tosylaminoacidate complexes with other metal ions such as Cd^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}, these systems will be the subject of future investigations.

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