# Copper(II) Complexes with *N*-Sulphonyl Amino Acids. Structure-Stability Relationships in Binary Species and Ternary Complexes with 2,2'-Bipyridine[†]

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The stability of a series of binary and ternary 2,2'-bipyridine(bipy) complexes of $Cu^{2+}$ with amino acids N-substituted by an arene sulphonic group has been analysed in 0.1 mol $dm^{-3}$ $NaClO_4$ or $NaNO_3$ at 25 °C. The stability constants determined by d.c. polarography are sensitive to the nature of the amino acid and of the aromatic moiety of the protecting group. The known lowering effect of bipy on the p*K* for metal-promoted sulphonamide nitrogen deprotonation in the ternary complexes is found to be quantitatively independent of the above structural features. The X-ray structure of the ternary species $[Cu(bipy)(Bs\text{-}GlyNO)(H_2O)]$ [Bs-GlyNO = *N*-benzenesulphonylglycinate(2−)] is also presented. The crystals are monoclinic, space group $P2_1/c$, with $a = 8.494(5)$, $= 19.950(4)$, $c = 11.295(7)$ Å, $\beta = 110.79(4)°$, $Z = 4$, and $R = 0.036$. The structure consists of $[Cu(bipy)(Bs\text{-}GlyNO)(H_2O)]$ units in which the Cu atom exhibits a tetrahedrally distorted square-pyramidal $N_3O_2$ co-ordination.

The effect of 2,2'-bipyridine (bipy) as an additional ligand in $M^{2+}$–*N*-$RSO_2$-amino acid complexes (M = Cu, Zn or Cd; R = aryl group) was previously investigated through d.c. polarography, pH-metric titrations, and $^1H$ NMR spectroscopy.[1a,2] The heteroaromatic base was invariably found to favour metal-promoted amide deprotonation of the amino acid ligand, unlike that observed in analogous ternary complexes with peptides.[3] In particular, a metal-co-ordinated bipy molecule turns out to be an essential requirement for the $Zn^{2+}$ ion to be effective in the proton displacement. In order to rationalize some aspects of this interaction, which must have molecular bases independent of the nature of the metal ion, we here report an investigation of this kind of ternary complexes formed by $Cu^{2+}$ with a number of *N*-$RSO_2$ amino acids having different R groups. In particular, we have characterized the species obtained in aqueous solution with Bs-Gly, Ts-β-Ala, Ts-Gly, and Dns-Gly through pH-metric and polarographic analyses (Gly = glycine, β-Ala = β-alanine; Bs = benzenesulphonyl, Ts = toluenesulphonyl, Dns = 5-dimethylaminonaphthalene-1-sulphonyl). We have chosen the $Cu^{2+}$ ion due to the conspicuous amount of analogous data available on its binary complexes with *N*-$RSO_2$ amino acids [1a,4,5] which are being used for comparative purposes. The aim of this work is to present an overall view of both binary and ternary (bipy) complexes formed by these *N*-substituted amino acids, with special emphasis on the lowering effect of bipy on the p*K* values for metal-promoted sulphonamide nitrogen deprotonation, and to outline the structure–stability relationships. In addition, the crystal and molecular structure of the ternary species $[Cu(bipy)(Bs\text{-}GlyNO)(H_2O)]$ [Bs-GlyNO = *N*-benzenesulphonylglycinate(2−)] is reported and compared with the corresponding binary complex, and with analogous ternary copper(II) complexes formed by other *N*-$RSO_2$-amino acids.

## Experimental

*Materials.*—Dns-Gly (Sigma), Ts-Gly, Bs-Gly and Ts-β-Ala were twice recrystallized before use. Doubly distilled water was used throughout. All chemicals were of the highest purity commercially available.

pH-*Metric and Polarographic Measurements.*—Potentiometric titrations of the binary systems $Cu^{2+}$–L, where L = Bs-Gly, Ts-Gly or Ts-β-Ala, were carried out on solutions containing $1 \times 10^{-3}$ mol $dm^{-3}$ metal ion $[Cu(ClO_4)_2]$, and ligand-to-metal molar ratios of 2:1 and 4:1. The ionic strength was adjusted to 0.1 mol $dm^{-3}$ with $NaClO_4$. Carbonate-free NaOH standardized against phthalate was used as a titrant. Measurements were performed on a fully automated Orion 960 Autochemistry system having a Ross 8102c combination electrode and operating under a nitrogen atmosphere at 25 ± 0.1 °C. The same experimental conditions were used for the pH-metric analysis of the ternary systems. A bipy:metal ratio of 1:1 was used throughout. Polarographic measurements on the $Cu^{2+}$–Bs-Gly and –Ts-β-Ala systems were carried out in aqueous solution with $5 \times 10^{-4}$ mol $dm^{-3}$ metal ion and ligand-to-metal molar ratios from 2:1 to 16:1. The same conditions were used for the analysis of the ternary systems where 2,2'-bipyridine was added in a 1:1 molar ratio with $Cu^{2+}$. The pH of the solution was adjusted by adding small amounts of concentrated aqueous NaOH. Sodium perchlorate was used as base electrolyte {$NaNO_3$ was used for the measurements on the system $Cu^{2+}$–Ts-β-Ala due to precipitation of the complex $[Cu(bipy)(OH)]ClO_4$} and the ionic strength was kept constant ($I$ = 0.1 mol $dm^{-3}$). Polarographic and voltammetric measurements were performed with an Amel 472 Multipolarograph at 25 ± 0.1 °C. A saturated calomel electrode (SCE) was used as reference and a platinum sheet as counter. All the $E_{\frac{1}{2}}$ values are referred to the SCE. Analysis of the electron-transfer processes was performed by using concentrations from $5 \times 10^{-5}$ to $5 \times 10^{-4}$ mol $dm^{-3}$ $Cu^{2+}$ (maintaining the same Cu:L and Cu:L:bipy molar ratios) and dropping times of 1,2,3,4 and 5 s. The reversibility of the processes was determined by semilogarithmic analysis of the polarographic waves and by voltammetric measurements

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[†] *Supplementary data available* (No. SUP 56844, 2 pp.): Lingane plots. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

**Table 1** Final positional parameters for [Cu(bipy)(Bs-GlyNO)($H_2O$)]

| Atom | *X/a* | *Y/b* | *Z/c* |
|---|---|---|---|
| Cu | 0.219 48(6) | 0.030 48(2) | 0.253 28(4) |
| N(1) | 0.123 7(4) | −0.048 4(2) | 0.309 9(3) |
| N(2) | 0.310 0(4) | 0.047 7(2) | 0.442 6(3) |
| C(1) | 0.030 4(6) | −0.096 0(2) | 0.235 0(4) |
| C(2) | −0.042 4(5) | −0.147 5(2) | 0.278 5(5) |
| C(3) | −0.017 4(6) | −0.149 6(2) | 0.404 4(5) |
| C(4) | 0.076 6(6) | −0.100 4(2) | 0.483 2(4) |
| C(5) | 0.148 6(5) | −0.050 8(2) | 0.435 5(4) |
| C(6) | 0.256 2(5) | 0.003 3(2) | 0.509 8(4) |
| C(7) | 0.303 3(6) | 0.009 2(2) | 0.640 2(4) |
| C(8) | 0.407 2(6) | 0.061 1(2) | 0.701 7(4) |
| C(9) | 0.464 4(5) | 0.105 7(2) | 0.632 4(4) |
| C(10) | 0.412 2(5) | 0.097 6(2) | 0.503 1(4) |
| O(1) | 0.197 0(4) | −0.015 3(1) | 0.096 8(3) |
| O(2) | 0.282 0(4) | −0.013 5(2) | −0.066 4(3) |
| C(11) | 0.273 8(5) | 0.011 3(2) | 0.030 6(4) |
| C(12) | 0.363 4(5) | 0.076 8(2) | 0.078 2(4) |
| N(3) | 0.318 7(4) | 0.102 6(1) | 0.184 5(3) |
| S | 0.287 4(1) | 0.180 12(5) | 0.187 2(1) |
| O(3) | 0.238 2(4) | 0.209 8(1) | 0.063 3(3) |
| O(4) | 0.177 0(4) | 0.191 8(1) | 0.257 6(3) |
| C(13) | 0.481 5(5) | 0.219 6(2) | 0.276 6(4) |
| C(14) | 0.489 5(6) | 0.265 4(2) | 0.368 5(4) |
| C(15) | 0.640 8(7) | 0.299 1(3) | 0.430 5(5) |
| C(16) | 0.781 2(6) | 0.284 2(3) | 0.402 2(5) |
| C(17) | 0.774 2(6) | 0.238 2(3) | 0.318 8(6) |
| C(18) | 0.622 5(6) | 0.205 6(2) | 0.248 5(5) |
| O(w) | −0.036 9(4) | 0.084 1(2) | 0.230 0(3) |

carried out at a scan rate of 100 mV $s^{-1}$ with a hanging mercury-drop electrode. Binary and ternary systems are characterized by reversible and quasi-reversible reduction processes, respectively. The reversible $E_{\frac{1}{2}}$ values for quasi-reversible processes, to be used in the determination of the overall stability constants, were obtained according to Matsuda and Ayabe.[6]

*Spectrophotometric Measurements.*—Electronic spectra were recorded with a Perkin-Elmer 551 spectrophotometer on solutions containing $2 \times 10^{-3}$ mol $dm^{-3}$ $Cu^{2+}$ (cell length = 1 cm). pH Titrations were performed by adding small volumes of concentrated NaOH solutions.

*Preparation of* [Cu(bipy)(Bs-GlyNO)($H_2O$)].—The compound was obtained by adding a methanolic solution (0.006 $dm^3$) of bipy ($10^{-2}$ mol $dm^{-3}$) to an aqueous solution (0.05 $dm^3$) of [Cu(Bs-GlyNO)($H_2O)_3$][7] ($1.2 \times 10^{-3}$ mol $dm^{-3}$). The solution was filtered and allowed to stand at room temperature (25 °C). After 24 h blue crystals of [Cu(bipy)(Bs-GlyNO)($H_2O$)] separated. Found: C, 47.95; H, 3.95; N, 9.45; S, 7.20. $C_{18}H_{17}CuN_3O_5S$: C, 47.95; H, 3.80; N, 9.30; S, 7.10%).

*X-Ray Data Collection and Structure Determination.*—*Crystal data.* $C_{18}H_{17}CuN_3O_5S$, $M = 450.955$, monoclinic space group $P2_1/c$, $a = 8.494(5)$, $b = 19.950(4)$, $c = 11.295(7)$ Å, $\beta = 110.79(4)°$, $U = 1789(2)$ Å$^3$, $D_m = 1.61$ g $cm^{-3}$, $Z = 4$, $D_c = 1.67$ g $cm^{-3}$, $F(000) = 924$, $\mu$(Mo-K$\alpha$) = 13.7 $cm^{-1}$, crystal size $0.20 \times 0.30 \times 0.25$ mm.

Cell dimensions were determined from least-squares refinement of the angular settings of 25 automatically centred reflections from different regions of reciprocal space. Intensity data were collected on an Enraf–Nonius CAD4 diffractometer at room temperature by using graphite-monochromated Mo-K$\alpha$ radiation ($\lambda = 0.710\,69$ Å) with the $\omega$–$2\theta$ scan technique, $\theta$ ranging from 2.5 to 25.0°, scan width $0.60 + 0.35 \tan\theta$, and scan speed 5.5–1.6° $min^{-1}$. Two standard reflections, monitored at 4 h intervals, were used as orientation and intensity test and showed no significant changes. The data were corrected for Lorentz and polarization effects. A total of 3392 independent reflections ($\pm h$, $+k$, $+l$) were measured of which 2552, having $I \geqslant 2\sigma(I)$, were used in the structure determination. The structure was solved by conventional Patterson and Fourier techniques, and refined through full-matrix least-squares calculations with $\Sigma w(|F_o| - |F_c|)^2$ being minimized. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on a Fourier difference map and were treated as fixed contributors with isotropic thermal parameters 1.0 Å$^2$ higher than those of the atoms to which they are bound. The weighting scheme $w = 1/[\sigma^2(F_o) + 0.0005\,F_o^{\,2}]$ led to final $R$ and $R'$ values of 0.036 and 0.042, respectively. During the last refinement zero weight was assigned to five reflections, which could be affected by extinction or by counting errors. Complex neutral atom scattering factors[8] were used throughout. Major calculations were carried out on a VAX 6310 computer using SHELX 76,[9] PARST[10] and ORTEP[11] programs. Final atomic coordinates are listed in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

## Results

*Binary Systems.*—The pH-metric titrations performed on Bs-Gly and Ts-Gly interacting with $Cu^{2+}$ are closely similar to those previously reported for Dns-Gly.[5] Two titration steps are observed. The former is known to correspond to the formation of a monohydroxo carboxylate complex [Cu(LO)(OH)], while the latter arises from deprotonation of the sulphonamide nitrogen of the ligand which, as a consequence, switches to a N,O-bidentate metal co-ordination through one carboxylic oxygen and the deprotonated sulphonamide nitrogen. Such a pH-dependent co-ordination mode was confirmed by polarographic and spectrophotometric studies of a number of systems $Cu^{2+}$–L, where L = Ts-Asn, Ts-Gln,[1a] Dns-Gly[5] or Ts-Gly.[4] On the other hand, only one titration step due to the neutralization of the carboxylate group of the ligand is observed for the system $Cu^{2+}$–Ts-β-Ala.

The compound Bs-Gly shows a polarographic titration pattern analogous to that exhibited by Ts-Gly,[4] with the appearance of two waves corresponding to carboxylate and N,O-bidentate complexes (in order of decreasing $E_{\frac{1}{2}}$ values), while only the wave corresponding to the carboxylate species is observed for Ts-β-Ala (not shown). The polarographic stability constants for the binary species formed by Bs-Gly, Ts-Gly and Ts-β-Ala reported in Table 2 were obtained analytically from the reversible $E_{\frac{1}{2}}$ values using the DeFord–Hume equation[13a] with a suitable computer program. Somewhat different values were determined previously for Ts-Gly,[4] most probably due to the graphical calculation procedure used at that time.

*Ternary Systems.*—Two titration steps appear in the pH-metric curve of the system $Cu^{2+}$–bipy–Ts-β-Ala. While the former clearly corresponds to neutralization of the carboxylic group of the ligand, the following could be attributed either to the formation of a stable monohydroxo species or to deprotonation of the sulphonamide nitrogen. The spectrophotometric pH titrations (see below) indicate that the latter is the case. The ternary systems involving Bs-, Ts- and Dns-Gly show only one pH-metric step corresponding to the second observed for Ts-β-Ala.

All the ligands invariably follow the same polarographic pattern, qualitatively similar to that observed for the binary system $Cu^{2+}$–Dns-Gly.[5] In the range pH 3–11 two waves are observed, both quasi-reversible, bielectronic and diffusion-controlled. The first wave (I) appears at pH values around 3 and completely disappears at pH 6.5–7. Its $E_{\frac{1}{2}}$ value is independent of pH. The second wave (II), at more negative potentials, grows starting from pH 5–6 and reaches its maximum intensity at pH 7–7.5. Again, the $E_{\frac{1}{2}}$ value is unchanged by pH. In the pH range of coexistence of both waves, wave II increases in intensity over

**Table 2** Values of log β for the prevailing binary and ternary copper(II) complexes[a] and p$K$ values for sulphonamide nitrogen deprotonation for free ligands and for binary and ternary systems in aqueous solution. $I$ = 0.1 mol dm$^{-3}$, 25 °C

| | | Ts-Gly | Bs-Gly | Dns-Gly | Ts-β-Ala | Ts-Gln | Ts-Asn |
|---|---|---|---|---|---|---|---|
| log β | $[Cu(LO)_2]$ | 5.2 | 5.3 | — | 5.5 | 4.4[b] | 4.3[b] |
| | $[Cu(LNO)]$ | 7.6 | 7.7 | 8.6[c] | — | 9.0[b] | 9.1[b] |
| | $[Cu(LNO)_2]^{2-}$ | 11.3 | 11.5 | 11.4[c] | — | 15.8[b] | 16.3[b] |
| | $[Cu(bipy)(LO)_2]$ | 13.3 | 13.4 | 13.6 | 13.7 | 12.4[b] | 12.5[b] |
| | $[Cu(bipy)(LNO)]$ | 16.1 | 16.2 | 17.1 | 14.7 | 17.6[b] | 17.7[b] |
| | $[Cu(bipy)(LNO)_2]^{2-}$ | 18.8 | 19.1 | — | — | 23.3[b] | 23.2[b] |
| $\Delta \log K$[d] | | 0.5 | 0.5 | 0.5 | — | 0.6[b] | 0.6[b] |
| p$K_{NH}$ | | 11.4 | 11.4 | 11.7 | 11.2 | 11.8 | 11.4 |
| p$K^{II}_{Cu(LNO)}$[e] | | 8.0 | 7.9 | 7.8[c] | — | 7.9 | 7.1 |
| p$K^{II}_{Cu(bipy)(LNO)}$[e] | | 5.5 | 5.2 | 5.0 | 6.6 | 5.1 | 4.7 |

[a] Overall stability constants (β) relative to the equilibrium $Cu^{2+} + m\ bipy + 2\ LO^-$ (or $n\ LNO^{2-}$) $\rightleftharpoons$ $[Cu(bipy)_m(LO)_2]$ or $[Cu(bipy)_m(LNO)_n]^{2-2n}$}, $m$ = 0 or 1 and $n$ = 1 or 2. The estimated error on log β is ±0.1. [b] From ref. 1*a*. [c] From ref. 5. [d] $\Delta \log K = \log K^{Cu(bipy)}_{Cu(bipy)(LNO)} - \log K^{Cu}_{Cu(LNO)}$; $\log K^{Cu}_{Cu(bipy)} = 8.0$.[12] [e] Apparent p$K_{NH}$ values for binary and ternary systems determined by electronic spectroscopy (see text).

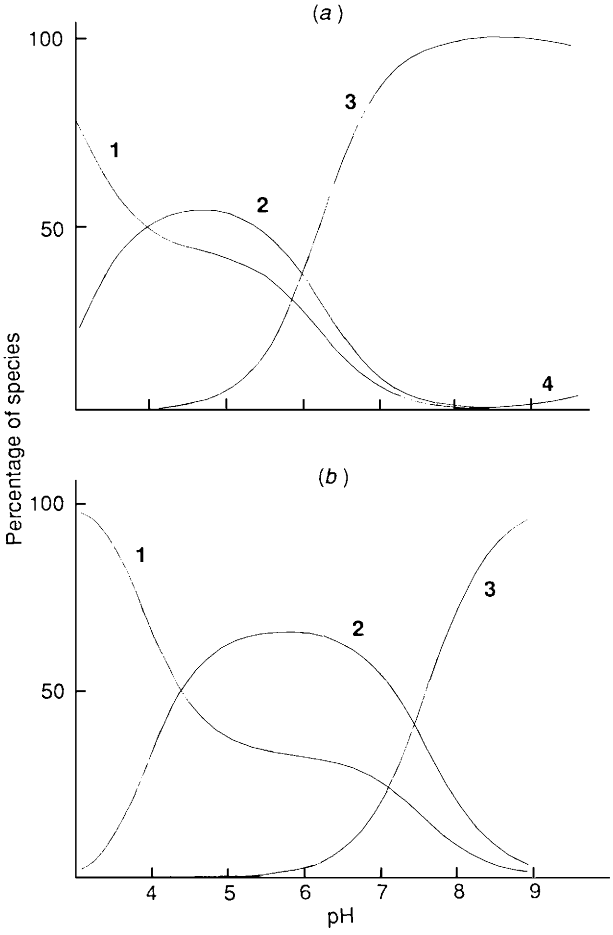

**Fig. 1** Species distribution curves for the ternary systems $Cu^{2+}$–L–bipy in a 1:4:1 molar ratio. L = Bs-Gly (*a*) or Ts-β-Ala (*b*). Species: **1**, $[Cu(bipy)]^{2+}$; **2**, $[Cu(bipy)(LO)_2]$; **3**, $[Cu(bipy)(LNO)]$; **4**, $[Cu(bipy)(LNO)_2]^{2-}$; $[Cu^{2+}] = 3 \times 10^{-3}$ mol dm$^{-3}$

wave I, but the overall current value remains constant. At pH > 9.5 the $E_{\frac{1}{2}}$ value of wave II becomes dependent on pH, thus indicating the formation of mixed-hydroxo complexes. Analogous polarographic behaviours were observed previously for the corresponding ternary systems involving Ts-Asn and -Gln.[1a] The overall stability constants for the prevailing ternary complexes, calculated from the reversible $E_{\frac{1}{2}}$ values with the method of Shaap and McMasters,[13b] are collected in Table 2, and the species distribution curves for Ts-β-Ala and Bs-Gly are reported in Fig. 1. Lingane plots[13c] indicate that complexes with a metal:ligand:bipy ratio of 1:2:1 invariably prevail when the ligand acts as a simple carboxylate while, upon metal-promoted amide deprotonation, 1:1:1 becomes the prevailing ratio. Two N-deprotonated ligand molecules are found to bind to the metal only at high ligand-to-metal ratios (>6:1) giving rise most probably to a species in which $Cu^{2+}$ is six-co-ordinate. The species $[Cu(bipy)(OH)]^+$ was not detected in any case.

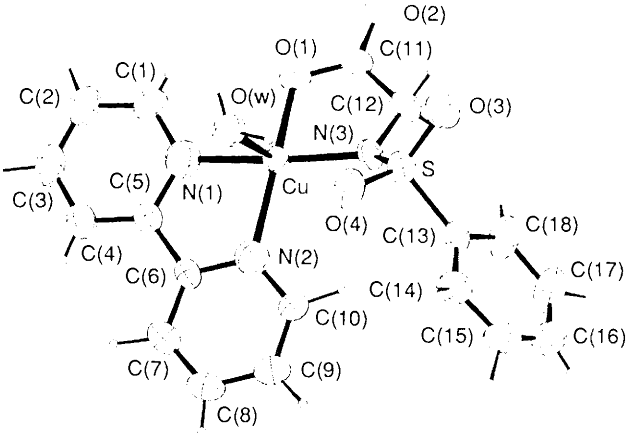

**Fig. 2** An ORTEP view of $[Cu(bipy)(Bs\text{-}GlyNO)(H_2O)]$ showing the atom numbering and the thermal motion ellipsoids (40%) for non-hydrogen atoms

The electronic spectra recorded as a function of pH invariably show an increase in intensity of the d–d band maximum of the $Cu^{2+}$ ion and a concomitant shift to higher energies (from 690–680 nm at pH about 3.5 to 680–660 nm at pH about 10, with Ts-β-Ala showing the greatest blue shift to 630 nm). The estimated apparent p$K_{NH}$ values are reported in Table 2. The compound Ts-β-Ala is the only ligand for which an isosbestic point is observed and its p$K_{NH}$ value was calculated accordingly.

*Structure of* $[Cu(bipy)(Bs\text{-}GlyNO)(H_2O)]$.—The crystal is comprised of hydrogen-bonded $[Cu(bipy)(Bs\text{-}GlyNO)(H_2O)]$ moieties in which the Cu atom exhibits a tetrahedrally distorted square-pyramidal $N_3O_2$ co-ordination. An ORTEP view with the labelling scheme is given in Fig. 2. The four basal ligands are the nitrogen atoms of the bipy molecule, the deprotonated sulphonamide nitrogen and one carboxylate oxygen of the Bs-Gly dianion; the apical position is occupied by the oxygen atom of the water molecule. The Cu–N and Cu–O equatorial distances (Table 3) are comparable to those observed for analogous ternary species formed by other $RSO_2$ amino acidate-NO dianions containing a $CuN_3O_2$ chromophore, *e.g.* tosylglycinate,[14] 5-dimethylaminonaphthalene-1-sulphonylglycinate,[15] tosyl-DL-asparaginate[1b] [mean Cu–$N_{eq}$ 1.99(1), Cu–$O_{eq}$ 1.95(1) Å]. The Cu–$O_{ax}$ bond distance is close to those found in the analogous adducts formed by Ts- and Dns-Gly,

**Table 3** Selected bond distances (Å) and angles (°)

| | | | |
|---|---|---|---|
| Cu–N(1) | 1.979(3) | N(2)–C(10) | 1.338(5) |
| Cu–N(2) | 2.029(3) | O(1)–C(11) | 1.269(6) |
| Cu–N(3) | 1.962(3) | O(2)–C(11) | 1.227(6) |
| Cu–O(1) | 1.938(3) | C(12)–N(3) | 1.473(6) |
| Cu–O(w) | 2.355(3) | N(3)–S | 1.572(3) |
| N(1)–C(1) | 1.330(5) | S–O(3) | 1.438(3) |
| N(1)–C(5) | 1.358(6) | S–O(4) | 1.448(4) |
| N(2)–C(6) | 1.348(6) | S–C(13) | 1.783(4) |
| N(1)–Cu–N(2) | 80.8(1) | Cu–N(1)–C(1) | 125.6(3) |
| N(1)–Cu–N(3) | 174.1(1) | Cu–N(1)–C(5) | 115.9(3) |
| N(1)–Cu–O(1) | 90.1(1) | Cu–N(2)–C(6) | 113.9(3) |
| N(1)–Cu–O(w) | 85.8(1) | Cu–N(2)–C(10) | 126.8(3) |
| N(2)–Cu–N(3) | 103.7(1) | Cu–N(3)–C(12) | 109.7(2) |
| N(2)–Cu–O(1) | 156.8(1) | Cu–N(3)–S | 127.9(2) |
| N(2)–Cu–O(w) | 91.7(1) | Cu–O(1)–C(11) | 115.8(3) |
| N(3)–Cu–O(1) | 84.3(1) | O(1)–C(11)–O(2) | 124.3(4) |
| N(3)–Cu–O(w) | 97.7(1) | S–N(3)–C(12) | 117.0(3) |
| O(1)–Cu–O(w) | 108.9(1) | | |

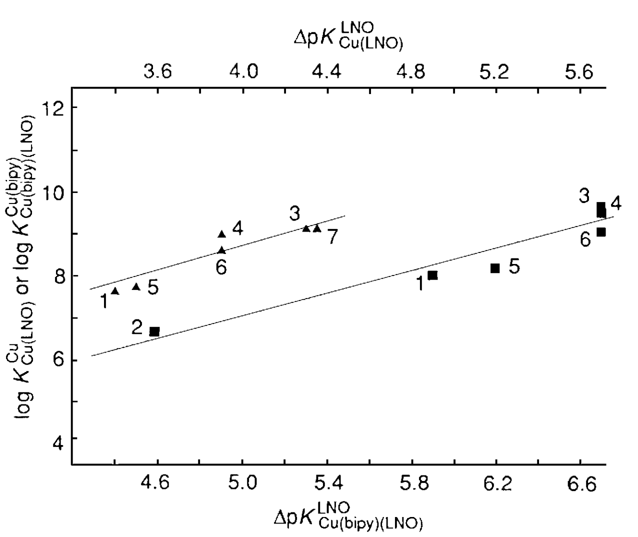

**Fig. 3** Plot of stability constants for binary and ternary species *vs.* the metal-induced decrease in the p$K$ value for sulphonamide nitrogen deprotonation. Upper line and upper abscissa: binary species. Lower line and lower abscissa: ternary species. $\Delta pK^{LNO}_{Cu(LNO)} = pK_{NH} - pK^{H}_{Cu(LNO)}$; $\Delta pK^{LNO}_{Cu(bipy)(LNO)} = pK_{NH} - pK^{H}_{Cu(bipy)(LNO)}$. Ligand L: Ts-Gly (1), Ts-β-Ala (2), Ts-Asn (3), Ts-Gln (4), Bs-Gly (5), Dns-Gly (6) or Ts-Leu (7) (from ref. 16)

while it is markedly shorter than that found in the Ts-Asn adduct[1b] (in this species the increased Cu–$O_{ax}$ bond length most probably arises from the strain induced by the tridentate chelating mode of Ts-Asn). In the present complex the four equatorial donor atoms show deviations from their least-squares mean plane (−0.154 to +0.184 Å) characteristic of a relevant tetrahedral distortion, as also indicated by the dihedral angle of 23.8(1)° between the mean planes of the two five-membered chelate rings, which turns out to be the greatest found to date in this kind of adduct (range: 8.8–14.5°).[1b,14,15] In addition, the square-pyramidal geometry is remarkably distorted, as indicated by the displacement of the copper ion from the mean co-ordination plane towards the apical water oxygen [0.216(1) Å] *cf.* range 0.064–0.208 Å for the above related complexes.[1b,14,15] The angle between the Cu–$O_{ax}$ vector and the normal to the mean equatorial plane is 9.4(1)° and falls in the range (7.4–10.5°) observed for the above-mentioned ternary complexes. The Cu–N and Cu–O bond distances are closely similar to those in the corresponding binary complex [Cu(Bs-GlyNO)$(H_2O)_3$] [Cu–N 1.966(4), Cu–O 1.936(3) Å];[7] the lengthening of apical Cu–O(w) in the bipy adduct may be attributed to the enhancement of in-plane bond strength ($CuN_3O_2$ chromophore *vs.* $CuNO_4$ in the binary species) which weakens the out-of-plane interaction. Bond distances and angles in the amino acid skeleton are those normally observed in copper(II) complexes of Bs-Gly.[7] Likewise, the structural parameters of the bipy molecule are normal, the two pyridine rings being planar within +0.011 to −0.074 Å and twisted by 2.98(1)° about the 2,2′ bond. The crystal packing is determined by stacking interactions between aromatic rings and the hydrogen bond involving the water molecule and the unco-ordinated carboxylic oxygen [O(w) ··· O($2^I$) 2.646(4), H(1w) ··· O($2^I$) 1.83 Å, O(w)–H(1w)–O($2^I$) 160°; I $-x, -y, -z$].

## Discussion

A collection of polarographic log β values for binary copper(II) complexes with N-protected amino acids is given in Table 2. As far as the factors influencing the metal-promoted sulphonamide nitrogen deprotonation in binary systems $Cu^{2+}$–*N*-$RSO_2$-amino acid are concerned, it is apparent that: (*i*) while the $pK_{NH}$ values of the free ligands are very similar, the corresponding N-deprotonated complexes M(LNO) show remarkably different stabilities: in other words, the different structural features of the side chains (of the amino acid moiety and of the N-protecting group as well) slightly affect the acidity of the NH group (Table 2), but are able to induce changes in the binding strength of the ligand upon nitrogen deprotonation; (*ii*) there is a fairly good correlation between the above stability constants and the metal-induced decrease in the p$K$ value for sulphonamide nitrogen deprotonation ($\Delta pK_{NH}$) (Fig. 3). As far as the former point is concerned, the order of stability for the binary complexes Cu(LNO), Ts-Asn ⩾ Ts-Gln > Dns-Gly > Bs-Gly ⩾ Ts-Gly, can be accounted for by the involvement of the amide oxygen of the amino acid side chain in metal co-ordination for the first two ligands[1a] {as observed in the X-ray structure of [Cu(bipy)(Ts-AsnNO)$(H_2O)$][1b]}, then by the greater dimensions of the aromatic group of Dns-Gly as compared to that of Ts- and Bs-Gly which, being conjugated with the metal co-ordination plane through the $SO_2$ group,[17] may increase the extent of a stabilizing π-delocalization. The above correlation between log β for the Cu(LNO) species and $\Delta pK_{NH}$ is a direct consequence of the competition between the metal ion and the proton for binding to the deprotonated sulphonamide nitrogen of the ligand.

As expected, no evidence for metal-promoted amide nitrogen deprotonation is obtained for Ts-β-Ala since this would involve the formation of an unfavoured six-membered chelate ring. On the other hand, Ts-β-Ala gives rise to the most stable carboxylate complexes, as is also observed for the interaction with $Cd^{2+}$,[18] owing to the greater basicity of the carboxylate group of Ts-β-Ala as compared to that of *N*-$RSO_2$-α-amino acids due to the lower extent of the electron-withdrawing effect exerted by the $SO_2$ group. The positive values (from 2 to 6) of log $[K^{Cu}_{Cu(LNO)}/K^{Cu(LNO)}_{Cu(LNO)_2}]$ displayed by all the N-protected amino acids so far investigated is worthy of note. The corresponding values observed for chelate copper(II) complexes of simple amino acids are in the range 1.2–1.7.[19] This remarkable difference is reasonably due to the negative charge of the $[Cu(LNO)_2]^{2-}$ species formed by the present ligands as compared to the neutrality of bis(amino acidato)copper(II) complexes. In addition, particularly in the case of Dns-Gly, the formation of the species bearing two N-deprotonated ligand molecules is unfavoured by the steric hindrance of the N-protecting group.

From Table 2 it is apparent that, independently of the ligand, the ternary carboxylate complexes are more stable than the corresponding binary species ($\Delta \log K \approx 0.1$), as previously observed for Ts-Asn and -Gln.[1a] Such an effect is characteristic of several carboxylate ligands, which invariably bind more strongly to the $[Cu(bipy)]^{2+}$ species than they do to the solvated metal ion.[3] Also the stabilizing effect of 2,2′-bipyridine on the N,O-bidentate species formed upon $Cu^{2+}$-promoted amide nitrogen deprotonation is fully confirmed: all the $\Delta\log K$ values are positive and fall in the range 0.5–0.6 (Table 2). The effect of the heteroaromatic base may be ascribed, as proposed previously,[1a,2] to the increased ability of the carboxylate group to act as primary ligating group[3] due to the above-mentioned stronger binding of carboxylate ligands to $[Cu(bipy)]^{2+}$ as compared to the aqua-ion, and to a stabilizing effect on the N,O-chelate species of the extensive π delocalization involving the aromatic ring of 2,2′-bipyridine and that of the N-protecting group. The lengthening of the apical Cu–O bond in the ternary complexes as compared to the binary species [2.355(3) *vs.* 2.270(3) Å for Bs-Gly[7] and 2.382(4) *vs.* 2.259(4) Å for Ts-Gly][14] is in line with this hypothesis. On passing from binary to ternary bipy complexes of a simple amino acid like glutamic acid[20,21] such an apical bond was found to shorten. The amide deprotonation observed for Ts-β-Ala in the ternary system indicates that these effects of bipy overcome the unfavoured formation of a six-membered chelate ring. The resulting complex, however, shows the lowest stability among the ternary [Cu(bipy)(LNO)] species, still due to the ring strain. A closely similar difference in stability is observed between the corresponding ternary bipy complexes formed by parent β-alanine and glycine.[22]

The correlation between the decrease in the $pK_{NH}$ values of the ligands upon metal binding in binary [Cu(LNO)] and ternary [Cu(bipy)(LNO)] systems ($\Delta pK_{NH}$) and the stability of the complexes (log $K$) is reported in Fig. 3. It is apparent that the relative stability of the species formed by different ligands is the same in binary and ternary systems. Hence, 2,2′-bipyridine does not introduce electronic and/or geometrical constraints able to modify the relative binding ability of such ligands, and exerts its effect independently of the side chain of the amino acid moiety and of the nature of the aromatic ring of the N-protecting group as well.

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