Ternary Copper(II) Complexes with 2,2′-Bipyridine and *N*-Tosyl-Substituted Amino Acids. Part 2.[1] Crystal and Molecular Structure of Aqua(2,2′-bipyridine)bis(*N*-tosyl-DL-asparaginato-*O*)copper(II) Dihydrate and (2,2′-Bipyridine)(*N*-tosyl-DL-asparaginato-*NO*)copper(II) Monohydrate

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The complexes [Cu(bipy)(tsasnO)$_2$(H$_2$O)]·2H$_2$O (**1**) and [Cu(bipy)(tsasnNO)]·H$_2$O (**2**) were separated from aqueous-alcoholic solutions at pH 4 and 6.4 respectively (tsasnO and tsasnNO = *N*-tosyl-DL-asparaginate monoanion and dianion respectively, bipy = 2,2′-bipyridine). The crystal and molecular structures were determined by *X*-ray diffraction. Compound (**1**) crystallizes in the space group $P\bar{1}$, with a = 18.162(4), b = 14.975(4), c = 7.272(2) Å, α = 103.67(6), β = 87.10(5), γ = 104.48(6)°, and Z = 2, while compound (**2**) crystallizes in the space group $P2_1/c$, with a = 12.421(9), b = 10.233(4), c = 17.773(7) Å, β = 101.65(2)° and Z = 4. In both compounds the copper atom exhibits a tetrahedrally distorted square-pyramidal geometry. In (**1**) the tsasnO monoanion acts as a monodentate carboxylate ligand leading to a CuN$_2$O$_3$ chromophore; in (**2**) the tsasnNO dianion acts as a tridentate ligand through the deprotonated sulphonamidic nitrogen, one carboxylic oxygen, and the amidic oxygen of the side chain, giving rise to a CuN$_3$O$_2$ chromophore.

The *X*-ray structural characterization of the ternary complexes [Cu(bipy)(tsasnO)$_2$(H$_2$O)]·2H$_2$O and [Cu(bipy)(tsasnNO)]·H$_2$O are reported (tsasnO and tsasnNO = *N*-tosylasparaginate monoanion and dianion respectively, bipy = 2,2′-bipyridine). These complexes were separated by following the indications obtained by the parallel solution study (Part 1).[1] The structural data are compared with other 2,2′-bipyridine–copper(II) ternary complexes of *N*-protected amino acids.[2–4] Some aspects of the co-ordinative ability of the asparaginate moiety are discussed.

Experimental

N-tosylasparagine (tsasn) was recrystallized from a 1 : 1 ethanol–water solution.

Preparation of Aqua(2,2′-*Bipyridine*)*bis*(N-*tosyl*-DL-*asparaginato*-O)*copper*(II) *Dihydrate*, [Cu(bipy)(tsasnO)$_2$(H$_2$O)]·2H$_2$O (**1**).—By mixing [Cu(tsasnO)$_2$]·2H$_2$O·2EtOH[5] (1 mmol) in hot water (60 cm^3) with a methanolic solution (6 cm^3) of bipy (1.67×10^{-2} mol dm^{-3}) a deep blue solution (pH ≈ 4) was obtained after stirring at ≈ 70 °C. The solution was filtered and cooled at room temperature (≈ 25 °C), and after 24 h. blue crystals of complex (**1**) separated (Found: C, 46.00; H, 4.70; N, 10.10; S, 7.70. Calc. for C$_{32}$H$_{40}$CuN$_6$O$_{13}$S$_2$: C, 45.50; H, 4.80; N, 10.00; S, 7.60%).

Preparation of (2,2′-*Bipyridine*)(N-*tosyl*-DL-*asparaginato*-NO)*copper*(II) *Monohydrate*, [Cu(bipy)(tsasnNO)]·H$_2$O (**2**).—Complex (**1**) (0.5 mmol) was suspended in water and treated while stirring with a few drops of aqueous KOH in order to obtain, after complete dissolution of the starting complex, the pH value of 6. Keeping the solution (120 cm^3) at room temperature overnight yielded blue-violet crystals of complex (**2**) (Found: C, 48.35; H, 4.40; N, 10.80; S, 6.00. Calc. for C$_{21}$H$_{22}$CuN$_4$O$_6$S: C, 48.30; H, 4.25; N, 10.70; S, 6.15%).

X-*Ray Data Collection*.—Crystals of both compounds were mounted in a random orientation on a Siemens AED four-circle computer controlled diffractometer; the resulting crystal data and other crystallographic details are reported in Table 1. Crystals of complex (**1**) slowly decompose and the data were corrected accordingly. Intensity data were corrected for Lorentz and polarization effects and put on absolute scale by least-squares. The structures were solved by the heavy-atom method and refined isotropically and anisotropically to convergence at R = 0.084 and 0.070 for complexes (**1**) and (**2**) respectively. For complex (**1**) the hydrogen atoms, placed in the calculated positions, were introduced in the last cycle of the refinement to R = 0.0638; the hydrogen atoms belonging to the water molecule and NH$_2$ groups were not calculated. In complex (**2**) the hydrogen atoms were located in ΔF synthesis and refined isotropically to R = 0.044. During the last refinement zero weight was assigned to 13 and 51 reflections, which could be affected by extinction or by counting errors, for complexes (**1**) and (**2**) respectively.

The final atomic co-ordinates are listed in Tables 2 and 3 for complexes (**1**) and (**2**) respectively; all calculations were performed using a GOULD 32/77 computer by using SHELX 76,[6] ORTEP,[7] and PARST[8] programs.

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

Analysis.—Carbon, hydrogen, nitrogen, and sulphur were analysed with a C. Erba Model 1106 elemental analyser.

Results and discussion

The structures of complexes (**1**) and (**2**), showing the labelling scheme, are shown in Figures 1 and 2 respectively. Selected bond distances and angles are reported in Tables 4 and 5 for complexes (**1**) and (**2**) respectively. Complex (**1**) consists of monomeric units of [Cu(bipy)(tsasnO)$_2$(H$_2$O)] and lattice

Table 1. Experimental data for the crystallographic analyses*

Compound	(1)	(2)
Formula	$C_{32}H_{40}CuN_6O_{13}S_2$	$C_{21}H_{22}CuN_4O_6S$
M	844.37	522.03
Space group	$P\bar{1}$	$P2_1/c$
a/Å	18.162(4)	12.421(9)
b/Å	14.975(4)	10.233(4)
c/Å	7.272(2)	17.773(7)
α/°	103.67(6)	90.0
β/°	87.10(5)	101.65(2)
γ/°	104.48(6)	90.0
U/Å^3	1 861(1)	2 212(2)
Z	2	4
D_c/g cm^{-3}	1.507	1.567
D_m/g cm^{-3}	1.52	1.58
No. of Reflections for lattice parameters $50 \leqslant \theta \leqslant 60°$	18	15
F(000)	878	1076
Crystal size/mm	0.36 × 0.49 × 0.55	0.42 × 0.36 × 0.53
μ/cm^{-1}	24.53	26.34
h range	−23—23	−22—22
k range	−19—19	0—13
l range	0—11	0—16
Standard reflection	7 8 1	0 1 7
No. of reflections measured	5578	3626
No. of reflections used in the refinement $[I > 3\sigma(I)]$	4412	2426
Min. and max. height in final Fourier difference map, $\Delta\rho$/ eÅ^{-3}	−0.54, 0.39	−0.51, 0.60
No. of refined parameters	595	386
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.0638	0.0440
$R' = [\Sigma w(\Delta F)^2/\Sigma wF^2_o]^{\frac{1}{2}}$	0.0725	0.0570
Weighting scheme parameters $K,g\{w = K[\sigma^2(F_o) + gF_o^2]\}$	1.22, 3.95 × 10^{-3}	2.51, 6.0 × 10^{-4}

* Details common to both compounds: temperature, 293K; Siemens AED diffractometer; Cu-K_α radiation; scan mode ω—2θ ($3 \leqslant \theta \leqslant 60°$); scan speed 6—12° min^{-1}; scan width 1.20 + 0.35 tanθ

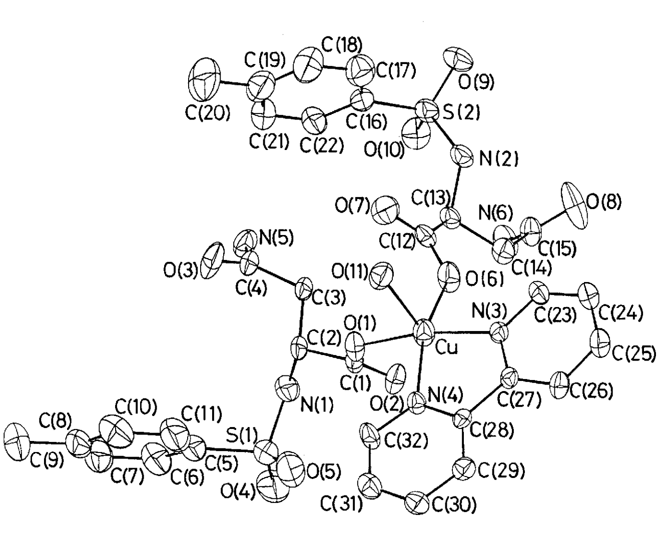

Figure 1. ORTEP view of the $[Cu(bipy)(tsasnO)_2(H_2O)]$ unit showing the atom numbering and thermal ellipsoids (40%) for non-H atoms

Table 2. Atomic co-ordinates (× 10^4) for $[Cu(bipy)(tsasnO)_2(H_2O)]\cdot 2H_2O$ (1) with estimated standard deviations (e.s.d.s) in parentheses

Atom	X/a	Y/b	Z/c
Cu	1 130.0(3)	2 024.9(5)	226.0(10)
S(1)	3 380.6(9)	951.9(12)	4 461.4(39)
S(2)	1 874.7(7)	6 294.7(9)	5 940.7(19)
O(1)	2 125(2)	2 065(3)	1 201(5)
O(2)	1 702(2)	1 804(3)	4 017(5)
O(3)	4 397(2)	4 004(3)	3 356(6)
O(4)	3 335(3)	596(5)	6 099(12)
O(5)	2 903(3)	443(3)	2 844(12)
O(6)	1 013(2)	3 097(3)	2 144(5)
O(7)	2 002(2)	4 297(3)	1 984(6)
O(8)	−221(3)	4 674(4)	7 661(6)
O(9)	1 538(2)	7 063(3)	5 980(7)
O(10)	2 100(2)	6 159(3)	7 678(6)
O(11)	1 657(2)	2 737(3)	−2 185(5)
O(12)	2 704(3)	4 702(4)	8 718(7)
O(13)	3 356(3)	2 984(5)	−821(8)
N(1)	3 240(2)	2 000(3)	5 034(7)
N(2)	1 248(2)	5 362(3)	4 954(6)
N(3)	43(2)	1 776(3)	−578(5)
N(4)	997(2)	719(3)	−1 411(5)
N(5)	4 174(2)	4 584(3)	6 421(7)
N(6)	765(3)	4 387(4)	8 909(7)
C(1)	2 216(2)	2 046(3)	2 930(7)
C(2)	3 047(2)	2 448(3)	3 638(7)
C(3)	3 148(2)	3 501(3)	4 468(8)
C(4)	3 960(3)	4 048(4)	4 713(8)
C(5)	4 319(3)	1 082(4)	3 652(12)
C(6)	4 899(4)	1 133(5)	4 840(13)
C(7)	5 633(4)	1 191(5)	4 116(14)
C(8)	5 809(4)	1 205(4)	2 281(14)
C(9)	6 612(4)	1 247(6)	1 556(16)
C(10)	5 214(5)	1 159(6)	1 081(15)
C(11)	4 482(4)	1 091(5)	1 736(14)
C(12)	1 460(3)	3 898(3)	2 777(7)
C(13)	1 284(3)	4 388(3)	4 815(7)
C(14)	543(3)	3 836(4)	5 536(7)
C(15)	332(3)	4 326(4)	7 472(7)
C(16)	2 685(3)	6 431(3)	4 497(8)
C(17)	2 653(4)	6 690(5)	2 807(10)
C(18)	3 302(4)	6 744(6)	1 641(11)
C(19)	3 947(4)	6 571(5)	2 172(11)
C(20)	4 645(5)	6 620(7)	864(15)
C(21)	3 973(3)	6 333(5)	3 855(11)
C(22)	3 348(3)	6 258(4)	5 049(9)
C(23)	−409(3)	2 381(4)	−82(8)
C(24)	−1 147(3)	2 151(4)	−681(8)
C(25)	−1 453(3)	1 257(4)	−1 766(8)
C(26)	−1 004(3)	613(4)	−2 253(7)
C(27)	−251(2)	897(3)	−1 653(6)
C(28)	295(2)	290(3)	−2 105(6)
C(29)	108(3)	−641(3)	−3 129(7)
C(30)	674(3)	−1 127(3)	−3 489(7)
C(31)	1 392(3)	−691(4)	−2 828(8)
C(32)	1 551(3)	241(4)	−1 783(7)

water molecules. The copper atom exhibits distorted square-pyramidal geometry with a N_2O_3 chromophore. The equatorial positions are occupied by the bipy molecule and two carboxylate oxygens of the two *N*-tosyl-DL-asparaginate mono-anions acting as monodentate ligands, and the apical one by one water molecule. The metal–ligand bond distances are in the ranges observed for other bipy adducts of copper(II)-*N*-protected aminoacidates with the chromophore CuN_2O_3: Cu–N 1.97—2.04, Cu–O 1.90—2.00, and Cu–O_{ax} 2.27—2.47 Å.[2,3]

In the co-ordination polyhedron the equatorial plane is tetrahedrally distorted with atomic deviations from −0.0383 to 0.0405 Å. The copper atom lies out of the basal plane by 0.200 Å

Table 3. Atomic co-ordinates (× 10^4) for [Cu(bipy)(tsasnNO)]·H_2O (**2**) with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Cu	3 168.8(7)	1 606.2(8)	2 214.9(5)
S	3 044.0(13)	1 410.8(15)	3 902.0(9)
O(1)	2 938(4)	3 481(4)	2 284(3)
O(2)	1 653(4)	4 839(5)	2 530(3)
O(3)	1 359(3)	1 556(4)	1 359(2)
O(4)	3 180(4)	2 666(4)	4 295(3)
O(5)	4 050(4)	731(5)	3 862(3)
O(6)	1 791(6)	448(6)	−41(4)
N(1)	4 250(4)	1 726(5)	1 524(3)
N(2)	3 398(5)	−294(5)	2 056(3)
N(3)	2 339(5)	1 490(5)	3 050(3)
N(4)	−176(6)	484(8)	1 466(4)
C(1)	2 836(7)	−1 277(7)	2 311(4)
C(2)	3 037(7)	−2 576(7)	2 165(5)
C(3)	3 845(7)	−2 869(7)	1 765(5)
C(4)	4 420(7)	−1 880(7)	1 509(5)
C(5)	4 177(5)	−578(6)	1 652(4)
C(6)	4 677(5)	560(6)	1 362(4)
C(7)	5 519(6)	493(7)	957(4)
C(8)	5 866(7)	1 637(7)	672(5)
C(9)	5 400(7)	2 801(8)	802(4)
C(10)	4 622(5)	2 817(6)	1 245(3)
C(11)	2 083(4)	3 743(5)	2 547(3)
C(12)	1 549(5)	2 588(5)	2 900(3)
C(13)	472(5)	2 133(7)	2 402(3)
C(14)	604(5)	1 362(5)	1 698(3)
C(15)	2 311(4)	405(5)	4 439(3)
C(16)	2 119(6)	770(7)	5 128(3)
C(17)	1 561(6)	−54(7)	5 542(4)
C(18)	1 219(5)	−1 263(6)	5 280(3)
C(19)	1 463(7)	−1 648(8)	4 607(4)
C(20)	1 996(7)	−830(7)	4 177(4)
C(21)	611(7)	−2 170(9)	5 717(5)

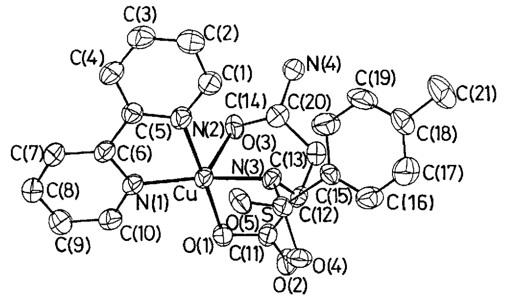

Figure 2. ORTEP view of the [Cu(bipy)(tsasnNO)] unit showing the atom numbering and thermal ellipsoids (40%) for non-H atoms

Table 4. Selected bond distances (Å) and angles (°) for [Cu(bipy)-(tsasnO)$_2$(H_2O)]·$2H_2O$ (**1**)

Cu–O(1)	1.956(4)	Cu–N(3)	2.005(4)
Cu–O(6)	1.910(4)	Cu–N(4)	1.998(4)
Cu–O(11)	2.309(4)	C(12)–O(6)	1.264(5)
C(1)–O(1)	1.284(7)	C(12)–O(7)	1.213(6)
C(1)–O(2)	1.233(6)	C(13)–N(2)	1.455(7)
C(2)–N(1)	1.441(8)	C(15)–O(8)	1.229(8)
C(4)–O(3)	1.235(7)	C(15)–N(6)	1.312(7)
C(4)–N(5)	1.326(7)	N(2)–S(2)	1.605(4)
N(1)–S(1)	1.607(5)	S(2)–O(9)	1.426(5)
S(1)–O(4)	1.406(10)	S(2)–O(10)	1.421(5)
S(1)–O(5)	1.437(7)	S(2)–C(16)	1.762(5)
S(1)–C(5)	1.754(6)		
O(1)–Cu–N(4)	94.2(2)	N(3)–Cu–O(6)	90.2(2)
O(1)–Cu–O(11)	92.9(2)	N(3)–Cu–O(11)	96.3(2)
O(1)–Cu–O(6)	92.9(2)	O(6)–Cu–O(11)	101.3(2)
N(4)–Cu–N(3)	80.4(2)	O(1)–Cu–N(3)	169.6(2)
N(4)–Cu–O(11)	93.0(2)	N(4)–Cu–O(6)	163.7(2)
Cu–N(4)–C(28)	116.0(4)	Cu–N(3)–C(23)	126.0(4)
Cu–N(4)–C(32)	124.7(4)	Cu–N(3)–C(27)	114.9(4)
Cu–O(1)–C(1)	121.4(4)	Cu–O(6)–C(12)	132.0(4)
O(1)–C(1)–O(2)	125.4(5)	O(6)–C(12)–O(7)	127.4(5)
O(3)–C(4)–N(5)	122.7(6)	O(8)–C(15)–N(6)	122.1(5)
O(3)–C(4)–C(3)	120.3(5)	N(6)–C(15)–C(14)	117.9(5)
N(5)–C(4)–C(3)	116.9(5)	C(14)–C(15)–O(8)	119.9(5)

Table 5. Selected bond distances (Å) and angles (°) for [Cu(bipy)-(tsasnNO)]·H_2O (**2**)

Cu–O(1)	1.948(4)	O(3)–C(14)	1.229(7)
Cu–O(3)	2.447(4)	N(4)–C(14)	1.324(9)
Cu–N(3)	1.974(6)	N(3)–C(12)	1.479(7)
Cu–N(1)	1.998(6)	N(3)–S	1.592(5)
Cu–N(2)	1.994(5)	S–O(4)	1.456(5)
O(1)–C(11)	1.272(8)	S–O(5)	1.444(5)
O(2)–C(11)	1.240(7)	S–C(15)	1.774(6)
O(1)–Cu–N(1)	96.0(2)	Cu–N(2)–C(1)	125.4(5)
O(1)–Cu–N(2)	175.5(2)	Cu–N(2)–C(5)	115.1(4)
O(1)–Cu–O(3)	86.1(2)	Cu–O(1)–C(11)	112.0(4)
O(1)–Cu–N(3)	84.6(2)	O(1)–C(11)–O(2)	124.7(5)
N(1)–Cu–N(2)	80.8(2)	Cu–O(3)–C(14)	113.2(3)
N(1)–Cu–O(3)	105.4(2)	O(3)–C(14)–N(4)	112.6(6)
N(1)–Cu–N(3)	169.6(2)	O(3)–C(14)–C(13)	122.7(5)
N(2)–Cu–O(3)	91.8(2)	N(4)–C(14)–C(13)	114.6(6)
N(2)–Cu–N(3)	99.0(1)	Cu–N(3)–C(12)	104.3(4)
O(3)–Cu–N(3)	85.0(2)	Cu–N(3)–S	116.6(3)
Cu–N(1)–C(6)	114.5(6)	S–N(3)–C(12)	115.3(4)
Cu–N(1)–C(10)	127.(4)		

towards the apical oxygen atom, the angle between the apical bond and the normal to the mean co-ordination plane being 4.5(1)°. Co-ordination only through the carboxylate group is typical of Cu^{II}–*N*–ArSO$_2$–aminoacidate complexes separated at acidic pH.[2] The carbonyl oxygen of the amide group of the amino acid side chain is not involved in co-ordination to the metal, unlike previously observed in the binary complexes given by the unsubstituted amino acid:[9] this is reasonably due to the electrophilic inductive effect of the tosyl group.

Crystals of complex (**2**) are composed of discrete molecular units of [Cu(bipy)(tsasnNO)] and lattice water molecules. The copper atom exhibits tetrahedrically distorted square-pyramidal co-ordination with the bipy molecule, carboxyl oxygen, and deprotonated sulphonamide nitrogen of the amino acid in the basal plane. The amidic oxygen occupies the apical position so that the tsasnNO dianion acts as a tridentate ligand forming a five- and six-membered chelate ring. The Cu–N and Cu–O equatorial distances are close to those found in copper(II) complexes of *N*-protected amino acids with a N_3O_2 chromophore, *e.g.* (2,2′-bipyridine)(ethanol)(*N*-tosylglycinato-*NO*) copper(II) (mean Cu–N_{eq} 1.981(5), Cu–O_{eq} 1.940(4) Å)[10] and (2,2′-bipyridine) (5-dimethylaminonaphthalene-1-sulphonylglycinato-*NO*)(methanol) copper(II) [mean Cu–N_{eq} = 1.97(1), Cu–O_{eq} = 1.97(1) Å].[4] The Cu–O_{ax} distance of 2.447(4) Å in the present complex, significantly longer if compared to the values of 2.37(1) and 2.382(4) Å for the above bipy complexes (where the apical ligands are alcoholic oxygens), is justified by the severely strained arrangement of tsasn. The four equatorial donor atoms show deviations (−0.122 to 0.135 Å) from the mean plane with the copper atom 0.064 Å out of this plane toward the apical oxygen. The

Table 6. Hydrogen bond distances (Å) and angles (°)

(*a*) [Cu(bipy)(tsasnO)$_2$(H$_2$O)]·2H$_2$O (**1**)

N(1)–H(6)	0.99(5)	N(2)–H(19)	0.73(6)
N(1) ··· O(13$^{\mathrm{I}}$)	3.018(8)	N(2) ··· O(8$^{\mathrm{II}}$)	2.712(7)
H(6) ··· O(13$^{\mathrm{I}}$)	2.03(5)	H(19) ··· O(8$^{\mathrm{II}}$)	2.00(5)
N(1)–H(6) ··· O(13$^{\mathrm{I}}$)	175(5)	N(2)–H(19) ··· O(8$^{\mathrm{II}}$)	165(5)

Short contacts which could be interpreted has hydrogen bonds

O(2) ··· O(11$^{\mathrm{I}}$)	2.792(5)	O(8) ··· N(6$^{\mathrm{V}}$)	2.823(7)
O(3) ··· N(5$^{\mathrm{III}}$)	2.894(6)	O(11) ··· O(12$^{\mathrm{IV}}$)	3.020(6)
O(7) ··· O(12$^{\mathrm{IV}}$)	2.761(7)	O(13) ··· N(1$^{\mathrm{IV}}$)	3.019(8)

(*b*) [Cu(bipy)(tsasnNO)]·H$_2$O (**2**)

O(6)–H(19)	0.82(6)	O(6)–H(20)	0.96(6)
O(6) ··· O(3)	2.882(8)	O(6) ··· O(4$^{\mathrm{VII}}$)	2.986(9)
H(19) ··· O(3)	2.09(6)	H(20) ··· O(4$^{\mathrm{VII}}$)	2.03(6)
N(4)–H(22)	0.91(6)	N(4)–H(21)	0.79(5)
N(4) ··· O(2$^{\mathrm{VI}}$)	2.88(1)	N(4) ··· O(6$^{\mathrm{VIII}}$)	3.049(9)
H(22) ··· O(2$^{\mathrm{VI}}$)	1.97(6)	H(21) ··· O(6$^{\mathrm{VIII}}$)	2.43(5)
O(6)–H(19) ··· O(3)	162(5)	O(6)–H(20) ··· O(4$^{\mathrm{VII}}$)	174(5)
N(4)–H(22) ··· O(2$^{\mathrm{VI}}$)	174(5)	N(4)–H(21) ··· O(6$^{\mathrm{VIII}}$)	135(5)

Equivalent positions: I $x, y, z + 1$; II $\bar{x}, 1 - y, 1 - z$; III $\bar{x} + 1, \bar{y} + 1, \bar{z} + 1$; IV $x, y, z - 1$; V $\bar{x}, 1 - y, 2 - z$; VI $\bar{x}, y - \frac{1}{2}, \bar{z} + \frac{1}{2}$; VII $x, \frac{1}{2} - y, z - \frac{1}{2}$; VIII $\bar{x}, \bar{y}, \bar{z}$.

angle between the Cu–O vector and the normal to the mean equatorial plane is 10.3(1)°.

The tridentate chelation mode of asparagine observed in complex (**2**) was suggested to be unfavoured due to the weak donor ability of the carbonyl oxygen of the neutral amide group which does not overcome the steric constraint of this ligand arrangement;[9] accordingly, in bis(L-asparaginato)copper(II)[9] the side chain bridges a second copper(II) ion. The axial co-ordination in complex (**2**) could be favoured by the strong square planar ligand field with the chromophore N$_3$O, in which a sizable π-back donation is present.[11] The amidic oxygen atom is preferred in the metal co-ordination with respect to the oxygen atom of the water molecule probably for steric reasons, but also because the water molecule is strongly involved in an extensive intermolecular network of hydrogen bonding which determines the crystal packing (Table 6).

In compound (**1**) hydrogen bond interactions involving co-ordinated and unco-ordinated water molecules, terminal amide groups and sulphonamide nitrogens (Table 6), and aromatic ring stacking interactions (ranging from 3.42 to 3.58 Å) among bipy ligands centrosymmetrically related, contribute to determine the crystal packing. The latter kind of interaction is absent in complex (**2**).

Bond distances and angles in the amino acid skeletal are in the range previously observed for the corresponding copper(II) complexes of *N*-tosyl derivatives showing both co-ordination modes,[2,10] as well as the shortening of S–N and lengthening of S–C bonds observed in complex (**2**) as compared with complex (**1**). In both compounds the C$^{\alpha}$–COO and the terminal amide group are roughly planar with bond distances and angles in the latter group being nearly identical. Finally, the two pyridine rings of bipy are nearly planar in both complexes and are twisted by 2.82 and 7.56° about the 2–2′ bond in complexes (**1**) and (**2**) respectively.

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