The Effect of a Dansyl Group on the Co-ordinative Ability of *N*-Protected Amino Acids. Part 2.[†] Binary Copper(II) Complexes and their Pyridine and 2,2′-Bipyridine Adducts. Crystal and Molecular Structure[‡] of the Complexes Aquabis(*N*-dansylglycinato-*O*)bis(pyridine)copper(II) and (2,2′-Bipyridine)-(*N*-dansylglycinato-*NO*)(methanol)copper(II), and Neutral *N*-Dansylglycine

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Some binary copper(II) complexes with *N*-dansylglycine (5-dimethylaminonaphthalene-1-sulphonylglycine) and their amine adducts with pyridine (py) and 2,2′-bipyridine (bipy) have been synthesized. Compounds of formula $Cu(dnsglyO)_2{\cdot}2CH_3OH$, $Cu(dnsglyO)_2{\cdot}4H_2O$, $[Cu(dnsglyO)_2(py)_2(H_2O)]$, and $[Cu(dnsglyNO)(bipy)(CH_3OH)]$ [dnsglyO = *N*-dansylglycinate(1−), dnsglyNO = *N*-dansylglycinate(2−)] were separated in the solid state and characterized by means of thermogravimetric, spectroscopic and magnetic measurements. For the free ligand and the amine adducts the crystal structure was also determined by the heavy-atom method and refined by least-squares calculations. The $[Cu(dnsglyO)_2(py)_2(H_2O)]$ complex is monoclinic, space group $P2/c$, with unit-cell dimensions a = 21.274(5), b = 5.719(5), c = 19.154(5) Å, β = 116.9(1)°, Z = 2; R = 0.061 for 1 845 observed reflections. The Cu^{II} ion, lying on the two-fold axis, is co-ordinated by two carboxylic oxygens of two symmetrically related amino-acid molecules and by two pyridine nitrogens in the basal plane of a tetragonal pyramid; the apical position is occupied by a water molecule, placed on the same two-fold axis at a very short distance from the Cu^{II} ion [Cu–O(5) 2.196(9) Å]. The $[Cu(dnsglyNO)(bipy)(CH_3OH)]$ complex is monoclinic, space group $P2_1$, with unit-cell dimensions a = 13.980(4), b = 11.087(3), c = 8.315(3) Å, β = 102.5(1)°, Z = 2; R = 0.085 for 1 160 observed reflections. The Cu^{II} ion displays tetrahedrally distorted square-pyramidal geometry arising from ligation of a $dnsglyNO^{2-}$ ion and a bipy molecule in the basal plane and of a methanolic oxygen in the apical position. *N*-Dansylglycine is monoclinic, space group $P2_1/n$, with unit-cell dimensions a = 21.653(5), b = 10.982(3), c = 5.935(2) Å, β = 93.51(8)°, Z = 4; R = 0.061 for 2 295 observed reflections. The ligand molecule is found to undergo conformational changes only upon amide deprotonation and the comparison with the structural results obtained for similar complexes of *N*-tosylglycine shows that the size of the aromatic group may have some influence on the co-ordination polyhedra.

α-Amino acids *N*-substituted by an $R{-}SO_2$ (R = aryl) group show in protic solvents a pH-dependent co-ordinative behaviour toward the copper(II) ion, as observed for a great variety of small peptide ligands.[1] Owing to the Cu^{II}-promoted deprotonation of the amide nitrogen atom, the $R{-}SO_2$ amino acids transform from *O*-carboxylate to *N,O*-bidentate ligands at pH values markedly lower than the pK_{NH} of the free amino-acid molecule. Both binding modes are retained in the solid state. In a previous investigation[2] about the interaction of *N*-dansylglycine (*N*-dansylglycine = 5-dimethylaminonaphthalene-1-sulphonylglycine) with the Cu^{II} ion in aqueous and methanolic solution we have determined the type, number, and stability constants of complexes present in solution over a wide pH range. The above change in the ligand co-ordination was observed in the pH ranges 7—8.5 and 8.5—11 in water and methanol[§] respectively. The comparison with the behaviour of the Cu–*N*-tosylglycinate system in the same solvents[4,5] revealed that the steric hindrance of the dansyl group could affect the ligand co-ordination number of complexes present in solution by inducing the prevalent formation of species with only one *N*-dansylglycine molecule bonded to the Cu^{II} ion. Now, in order to verify if and how the size of the R group affects the geometry and the metal-to-ligand molar ratio of the solid-state complexes, binary Cu^{II}–*N*-dansylglycinate complexes and their pyridine (py) and 2,2′-bipyridine (bipy) adducts were separated in the solid state, characterized by means of magnetic and spectroscopic measurements and discussed in comparison with the Cu^{II}–*N*-tosylglycinate complexes previously described.[4a] Only crystals of the ternary complexes were found suitable for *X*-ray structural analysis which was also carried out for *N*-dansylglycine with the aim of revealing whether the amino-acid molecule undergoes conformational changes upon metal ion co-ordination.

[†] Part 1 is ref. 2.

[‡] *Supplementary data available* (No. SUP 56496, 12 pp.): all thermal parameters, H-atom co-ordinates, complete bond distances and angles, intermolecular contacts, experimental and calculated corrected molar susceptibilities and magnetic moments. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non-S.I. units employed: B.M. = 9.274×10^{-24} J T^{-1}, G = 10^{-4} T.

[§] The pH values of the methanolic solution reported in this paper are referred to the pH scale in methanol. The measurements in mixed aqueous–methanolic solution, up to a water–methanol ratio of 1:1, were performed with pH combined electrode standardized in aqueous solution.[3]

Table 1. Crystal data

Compound	$[Cu(dnsglyO)_2(py)_2(H_2O)]$	$[Cu(dnsglyNO)(bipy)(CH_3OH)]$	*N*-Dansylglycine
Formula	$C_{38}H_{42}CuN_6O_9S_2$	$C_{25}H_{26}CuN_4O_5S$	$C_{14}H_{16}N_2O_4S$
M	854.5	558.1	308.4
Space group	$P2/c$	$P2_1$	$P2_1/n$
a/Å	21.274(5)	13.980(4)	21.653(5)
b/Å	5.719(5)	11.087(3)	10.982(3)
c/Å	19.154(5)	8.315(3)	5.935(2)
β/°	116.9(1)	102.5(1)	93.51(8)
U/Å^3	2 078(2)	1 258.2(8)	1 408.7(7)
Z	2	2	4
D_c/g cm^{-3}	1.37	1.47	1.45
D_m/g cm^{-3} (by flotation)	1.36	1.45	1.44
Reflection for lattice parameters	20	20	20
θ range (°)	20—23	60—70	60—70
Radiation	Mo-K_α	Cu-K_α	Cu-K_α
Wavelength (Å)	0.710 688	1.541 78	1.541 78
F(000)	890	578	648
T/K	293	293	293
Crystal size (mm)	0.70 × 0.33 × 0.55	0.25 × 0.36 × 0.42	0.13 × 0.49 × 0.54
Diffractometer	Siemens AED	Siemens AED	Siemens AED
μ/cm^{-1}	6.78 (Mo-K_α)	23.2 (Cu-K_α)	21.6 (Cu-K_α)
Scan speed (° min^{-1})	2.5	2.5	2.5
Scan width (°)	$1.20 + 0.35\ \text{tg}\theta$	$1.20 + 0.35\ \text{tg}\theta$	$1.20 + 0.35\ \text{tg}\theta$
θ range (°)	3—23	3—60	3—70
Reflections measured	3 240	2 140	3 116
Condition for observed	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 3\sigma(I)$
Reflections used in the refinement	1 845	1 160	2 295
Parameters	300	304	254
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.061	0.085	0.061
$R' = \lvert\Sigma w(\Delta F)^2/\Sigma wF_o^2\rvert^{\frac{1}{2}}$	0.064	0.086	0.063
$k, g\ [w = k/\sigma^2(F_o) + g\,F_o^2]$	0.9039, 0.003 79	0.8194, 0.015 64	1, 0.0078

Experimental

All chemicals were reagent grade and used without further purification.

Preparation of Binary Complexes.—Green crystals of empirical formula $Cu(dnsglyO)_2 \cdot 2CH_3OH$ [dnsglyO = *N*-dansylglycinate(1 −)] were rapidly obtained by evaporation at room temperature of a concentrated methanolic solution containing copper(II) acetate (0.2 mol dm^{-3}) and amino acid in a 1:2 molar ratio at pH 7.5 (Found: C, 47.45; H, 4.55; N, 7.40; S, 8.60; CH_3OH, 9.20. Calc. for $C_{30}H_{38}CuN_4O_{10}S_2$: C, 48.55; H, 5.15; N, 7.55; S, 8.65; CH_3OH, 8.60%). The elemental analysis is referred to the freshly prepared compound, as are the physical measurements reported below, since the solvent content has been found to decrease with time due to the solvent loss at room temperature (see thermogravimetric data below).

A compound of empirical formula $Cu(dnsglyO)_2 \cdot 4H_2O$ has been obtained from an aqueous methanolic solution (4:1) at pH 6 containing *N*-dansylglycine and freshly prepared $Cu(OH)_2$ in a 2:1 molar ratio; after some hours of stirring, the undissolved $Cu(OH)_2$ was filtered off. By slowly evaporating the solution at room temperature, pale blue crystals separated (Found: C, 44.7; H, 4.95; N, 7.40; S, 8.55; H_2O, 9.60. Calc. for $C_{28}H_{38}CuN_4O_{12}S_2$: C, 44.8; H, 5.10; N, 7.45; S, 8.55; H_2O, 9.60%).

Preparation of Aquabis(N-*dansylglycinato*-O)*bis*(*pyridine*)*copper*(II), $[Cu(dnsglyO)_2(py)_2(H_2O)]$, *and* (2,2′-*Bipyridine*)(N-*dansylglycinato*-NO)(*methanol*)*copper*(II), $[Cu(dnsglyNO)(bipy)(CH_3OH)]$.—Both complexes were obtained by adding to an aqueous methanolic solution (1:1) of the green compound a slight excess of pyridine and 2,2′-bipyridine respectively. The blue solutions obtained were evaporated at room temperature and after nearly 8 h blue crystals separated {Found: C, 52.85; H, 4.75; N, 9.60; S, 7.25; H_2O, 2.30. Calc. for $[Cu(dnsglyO)_2(py)_2(H_2O)]$ ($C_{38}H_{42}CuN_6O_9S_2$): C, 53.4; H, 4.95; N, 9.85; S, 7.50; H_2O, 2.10%. Found: C, 53.25; H, 4.70; N, 10.1; S, 5.50; CH_3OH, 6.30. Calc. for $[Cu(dnsglyNO)(bipy)(CH_3OH)]$ ($C_{25}H_{26}CuN_4O_5S$): C, 53.8; H, 4.70; N, 10.05; S, 5.75; CH_3OH, 5.75%}.

Physical Measurements.—Diffuse reflectance spectra were recorded with a Varian Cary 2300 spectrophotometer. The i.r. spectra were recorded with Perkin-Elmer 521 and Perkin-Elmer 180 spectrophotometers as KBr pellets and as Nujol mulls on KBr as support in the 4 000—250 cm^{-1} spectral range. The e.s.r. spectra were recorded with a Bruker ER 200 D-SRC spectrometer on polycrystalline samples with diphenylpicrylhydrazyl (dpph, g = 2.0036) as calibrant and field marker. Magnetic susceptibility measurements were obtained on a Newport Instruments magnetic (Gouy) balance employing a Newport Instruments cryostatic cooling system, with $Hg[Co(SCN)_4]$ as calibrant, and were corrected for diamagnetism with the appropriate Pascal constants.

Analyses.—Sulphur, nitrogen, carbon, and hydrogen were analysed with a C.Erba Elemental Analyser model 1106 by Mr. G. Goldoni. The water and methanol content were determined gravimetrically with thermal analyses performed at a rate of 5 °C min^{-1} with a Mettler TA3000 instrument.

X-*Ray Data Collection.*—The relevant data concerning the crystal structure analyses are summarized in Table 1. The intensities were collected with a Siemens AED diffractometer using Cu-K_α radiation for $[Cu(dnsglyNO)(bipy)(CH_3OH)]$ and *N*-dansylglycine and Mo-K_α radiation for $[Cu(dnsglyO)_2(py)_2(H_2O)]$, and the $\omega - 2\theta$ scan technique with individual profile analysis. One reflection was measured every 50 reflections as a check of the alignment of the crystal and

Table 2. Fractional atomic co-ordinates ($\times 10^4$) with e.s.d.s in parentheses for $[Cu(dnsglyO)_2(py)_2(H_2O)]$

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu	0	2 072(3)	2 500	C(8)	-3 733(6)	4 566(34)	1 349(8)
O(5)	0	5 912(16)	2 500	N(2)	-4 230(5)	3 674(28)	1 597(6)
O(1)	-751(3)	2 166(11)	1 425(3)	C(11)	-3 326(9)	6 410(37)	1 687(9)
C(1)	-1 088(5)	404(20)	1 075(5)	C(12)	-2 819(10)	7 224(32)	1 449(7)
O(2)	-987(4)	-1 648(13)	1 289(4)	C(13)	-2 745(7)	6 176(21)	843(6)
C(2)	-1 715(6)	789(18)	273(7)	C(14)	-3 191(5)	4 294(20)	447(5)
N(1)	-1 827(4)	3 300(14)	62(5)	N(3)	744(4)	1 647(14)	2 112(5)
S	-2 606(1)	3 999(4)	-589(1)	C(15)	1 265(5)	3 185(22)	2 338(7)
O(3)	-2 764(3)	2 556(11)	-1 256(3)	C(16)	1 773(7)	3 001(26)	2 077(9)
O(4)	-2 618(4)	6 461(10)	-676(4)	C(17)	1 785(6)	1 080(23)	1 651(7)
C(3)	-3 192(5)	3 171(18)	-209(5)	C(18)	1 275(7)	-533(25)	1 464(8)
C(4)	-3 618(5)	1 297(22)	-557(7)	C(19)	747(6)	-178(20)	1 684(7)
C(5)	-4 102(7)	538(35)	-298(9)	C(10a)[a]	-4 460(15)	5 995(53)	1 969(17)
C(6)	-4 143(6)	1 480(31)	320(9)	C(10b)[b]	-4 887(19)	4 502(65)	1 235(23)
C(7)	-3 689(6)	3 434(25)	709(6)	C(9)[c]	-3 959(10)	2 350(33)	2 242(12)

[a] Estimated population 0.60. [b] Estimated population 0.52. [c] Estimated population 0.88.

Table 3. Fractional atomic co-ordinates ($\times 10^4$) with e.s.d.s in parentheses for $[Cu(dnsglyNO)(bipy)(CH_3OH)]$

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu	165(1)	2 500*	2 088(2)	S	-2 156(2)	2 823(3)	1 586(4)
N(1)	1 351(7)	2 550(10)	1 160(10)	O(3)	-1 970(8)	3 650(10)	410(10)
C(1)	1 860(10)	1 590(10)	770(20)	O(4)	-2 879(7)	1 900(10)	940(10)
C(2)	2 690(10)	1 670(20)	210(20)	C(13)	-2 630(10)	3 620(10)	3 120(10)
C(3)	3 020(10)	2 830(20)	-10(20)	C(14)	-2 120(10)	3 610(10)	4 680(20)
C(4)	2 560(10)	3 850(20)	400(20)	C(15)	-2 460(10)	4 180(20)	5 910(20)
C(5)	1 710(10)	3 670(10)	950(20)	C(16)	-3 310(20)	4 770(20)	5 560(30)
C(6)	1 100(10)	4 660(10)	1 430(10)	C(17)	-3 880(10)	4 850(20)	3 890(20)
C(7)	1 390(10)	5 830(10)	1 400(20)	C(18)	-4 740(20)	5 540(20)	3 460(40)
C(8)	780(10)	6 710(20)	1 900(20)	C(19)	-5 290(20)	5 560(20)	1 950(40)
C(9)	-60(10)	6 340(20)	2 440(20)	C(20)	-4 950(20)	4 970(20)	680(20)
C(10)	-250(10)	5 110(20)	2 460(20)	C(21)	-4 110(10)	4 310(10)	1 010(20)
N(2)	311(8)	4 250(10)	1 940(10)	C(22)	-3 540(10)	4 250(10)	2 620(20)
O(1)	275(8)	730(10)	2 300(10)	N(4)	-5 130(20)	6 000(30)	4 990(40)
O(2)	-334(8)	-831(9)	3 290(10)	C(23)	-4 660(20)	7 150(50)	5 640(70)
C(11)	-350(10)	210(10)	2 950(20)	C(24)	-6 210(30)	6 140(50)	4 710(90)
C(12)	-1 210(9)	990(10)	3 190(10)	O(5)	1 150(10)	2 780(10)	4 760(10)
N(3)	-1 154(8)	2 201(9)	2 450(10)	C(25)	2 050(20)	2 470(40)	5 360(40)

* The origin of the unit cell was arbitrarily defined by assigning a value of 0.25 to the *y* co-ordinate of the Cu atom.

instrument stability. The structure amplitudes were obtained after the usual Lorentz and polarization reduction and converted to an absolute scale by least squares. No correction for absorption was applied. For the py adduct the μR value is very low (0.11) and the absorption coefficient is invariant over the range of θ values 3—23° ($A^* = 1.20$) assuming a cylindrical shape for the crystal. For *N*-dansylglycine and the bipy adduct ($\mu R = 0.35$, $A^* = 1.80$—1.71 in the θ range 3—70°) the correction for absorption did not give an appreciable improvement of the *R* index.

Solution and Refinement of the Structures.—The structures were solved by the heavy-atom technique and refined by least squares. For the py adduct, Cu, S, O, and N were refined anisotropically excluding the two *N*-methyl carbon atoms which were disordered and located in three different positions with populations 0.52, 0.60, and 0.88. The hydrogen atoms, excluding those belonging to the *N*-methyl groups were included in the final refinement with isotropic thermal parameters. For the bipy adduct anisotropic refinement was carried out for Cu, S, O, N, and C excluding the two *N*-methyl and methanolic carbon atoms which were refined isotropically. Hydrogen atoms were included in the structure factors in calculated positions; only the hydrogen belonging to the hydroxyl group of methanol was omitted. 18 Reflections (−5 −9 2, 0 −1 3, −10 −8 4, −8 −8 4, −7 −8 4, −6 −8 4, −11 −4 4, −11 −2 4, −11 0 4, 1 −5 7, 4 −5 7, −4 −3 7, 1 −1 7, −9 0 7, −8 0 7, −4 0 7, −3 0 7, 1 0 7) affected by extinction or counting errors were excluded from the final refinement. For *N*-dansyglycine, after anisotropic refinement of S, O, N, and C, the hydrogen atoms were localized from a ΔF map and refined isotropically. 15 Reflections (6 0 0, 1 0 1, 4 0 0, 8 0 0, 0 2 0, 2 3 0, −1 1 1, −1 0 1, −3 2 1, 5 1 1, 5 0 1, 7 0 1, −5 0 5, −3 0 5, 1 0 5) affected by extinction or counting errors were excluded from the final refinement.

The atomic scattering factors used, corrected for anomalous dispersion, were taken from International Tables.[6] All the calculations were performed by using the CYBER 76 computer of the Centro di Calcolo dell'Italia Nord-Orientale, Bologna, with the SHELX 76 program package[7] and the ORTEP plotting program.[8] The final non-hydrogen atomic parameters with their estimated standard deviations are listed in Tables 2—4.

Results and Discussion

As previously observed for a great variety of *N*-protected amino acids in aqueous and alcoholic media,[4,5] *N*-dansylglycine reacts with Cu^{II} ion, producing solvated complexes. In particular, two

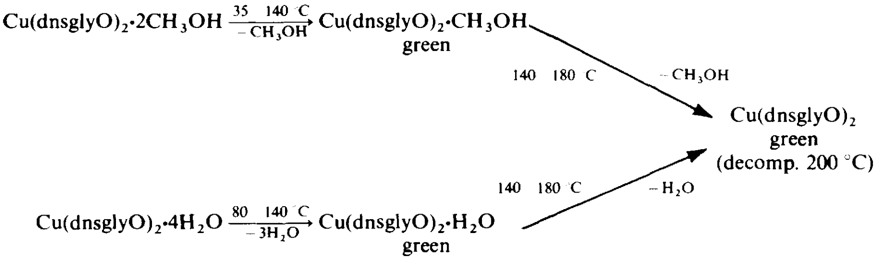
Table 4. Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for *N*-dansylglycine

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
S	4 061(0)	7 446(0)	5 947(1)	C(5)	2 582(1)	8 220(2)	1 764(4)
O(1)	4 129(1)	3 817(2)	4 439(3)	C(6)	2 094(1)	7 698(2)	2 744(4)
O(2)	4 196(1)	4 056(2)	707(3)	C(7)	2 181(1)	6 996(2)	4 750(4)
O(3)	4 053(1)	7 540(2)	8 340(3)	C(8)	2 797(1)	6 815(2)	5 742(4)
O(4)	4 394(1)	8 341(2)	4 741(3)	C(9)	2 885(1)	6 025(2)	7 606(4)
N(1)	4 356(1)	6 132(2)	5 395(4)	C(10)	2 394(1)	5 444(2)	8 479(4)
N(2)	1 044(1)	6 716(2)	4 927(3)	C(11)	1 784(1)	5 658(2)	7 595(4)
C(1)	4 229(1)	4 436(2)	2 803(5)	C(12)	1 671(1)	6 433(2)	5 793(4)
C(2)	4 397(1)	5 772(2)	3 053(4)	C(13)	851(1)	5 972(3)	2 920(5)
C(3)	3 285(1)	7 464(2)	4 723(4)	C(14)	568(1)	6 582(3)	6 625(5)
C(4)	3 183(1)	8 122(2)	2 776(4)				

Table 5. Physical data and room temperature (298 K) magnetic, e.s.r., electronic, and i.r. data for *N*-dansylglycine and its copper(II) complexes

Parameter	dnsgly	$Cu(dnsglyO)_2\cdot 2CH_3OH$	$Cu(dnsglyO)_2\cdot 4H_2O$	$[Cu(dnsglyO)_2(py)_2(H_2O)]$	$[Cu(dnsglyNO)(bipy)(CH_3OH)]$[a]
$\mu_{eff.}$(298 K)		1.70[b]	1.87	1.89	1.87
$\mu_{eff.}$(111 K)		0.86[b]			
$g_{\parallel}$		2.40[c,d]	$g_2 = 2.11$, $g_3 = 2.06$		2.24
$g_{\perp}$		2.11	$g_1 = 2.31$		2.07
$\langle g \rangle$		2.21	2.16	$g_{iso} = 2.09$	2.13
D/cm^{-1}		0.36			
$\lvert 2J \rvert$/cm^{-1}		206 ± 16[c]			
d–*d* transition, ν/cm^{-1}		11 300(sh), 13 700	13 500	12 700(sh), 15 500	14 600, 16 400(sh)
ν(OH)/cm^{-1}		3 500vs	3 500vs	3 450s br	3 450m br
ν(NH)/cm^{-1}	3 280	3 280s	3 280s	3 300s	
ν$(OCO)_{asym}$/cm^{-1}	1 700	1 615vs, 1 650vs	1 620vs	1 600vs	1 600vs
ν$(OCO)_{sym}$/cm^{-1}	1 418vs	1 410vs	1 410vs	1 390vs	1 375s
ν$(SO_2)_{asym}$/cm^{-1}	1 345vs	1 315vs	1 320vs	1 320vs	1 250vs
ν$(SO_2)_{sym}$/cm^{-1}	1 150vs, 1 175vs	1 145vs	1 142vs	1 135, 1 155vs	1 125, 1 100vs
ν(SN)/cm^{-1}	885vs	865vs	875vs	890s	910s

[a] Bands at 1 300ms and 1 055ms cm^{-1} are assigned to bending of the OH and C–O group respectively of the co-ordinated methanol molecule. [b] Values corrected for the presence of monomeric species with an estimated molar fraction of 0.27. [c] All the e.s.r. parameters are unchanged at 167 K. [d] E.s.r. parameters for monomer: $g_{\parallel} = 2.37$, $g_{\perp} = 2.08$, $\langle g \rangle = 2.18$; $A = 193 \times 10^{-4}$ cm^{-1}.



Scheme.

crystalline complexes, one green of empirical formula $Cu(dnsglyO)_2\cdot 2CH_3OH$ and the other pale blue of empirical formula $Cu(dnsglyO)_2\cdot 4H_2O$, were obtained from a methanolic and an aqueous–methanolic (4:1) solution respectively. As they were found to modify on *X*-ray exposure, their diffractometric structural analysis was not performed. Their thermal behaviour is very similar and can be represented by the Scheme. The spectroscopic and magnetic properties of these complexes are reported in Table 5 and suggest for the pale blue compound the presence of discrete monomeric species with a CuO_6 chromophore.[9] The green compound shows typical properties of a dimeric copper(II) acetate-like structure with exchange coupled pairs, as previously found for other *N*-protected amino acids.[5] In particular, the e.s.r. spectra show, in addition to the three absorptions assigned to transitions in the triplet state, a strong absorption near 3 000 G whose intensity increases with decreasing temperature; this indicates the presence of a monomeric species for which an estimated mol fraction of 0.27 was obtained from the fitting process of the magnetic susceptibility data. Therefore, though the magnetic susceptibility of the green compound might be satisfactorily described by a conveniently modified Bleaney-Bowers equation,[10] the $\lvert 2J \rvert$ value of 206 ± 16 cm^{-1}, calculated by the least-squares procedure, being out of the range (272—351 cm^{-1}) for *N*-protected amino acids,[11] cannot be used to evaluate the strength but only to support the presence of Cu–Cu interactions. In both binary complexes, the i.r. absorption frequencies of the SO_2 group are unchanged from those of the free ligand, excluding the involvement of this group in metal ion co-ordination.

Pyridine and 2,2′-bipyridine easily react with the above compounds in aqueous methanolic (1:1) solution, yielding ternary complexes. Though both reactions take place at pH

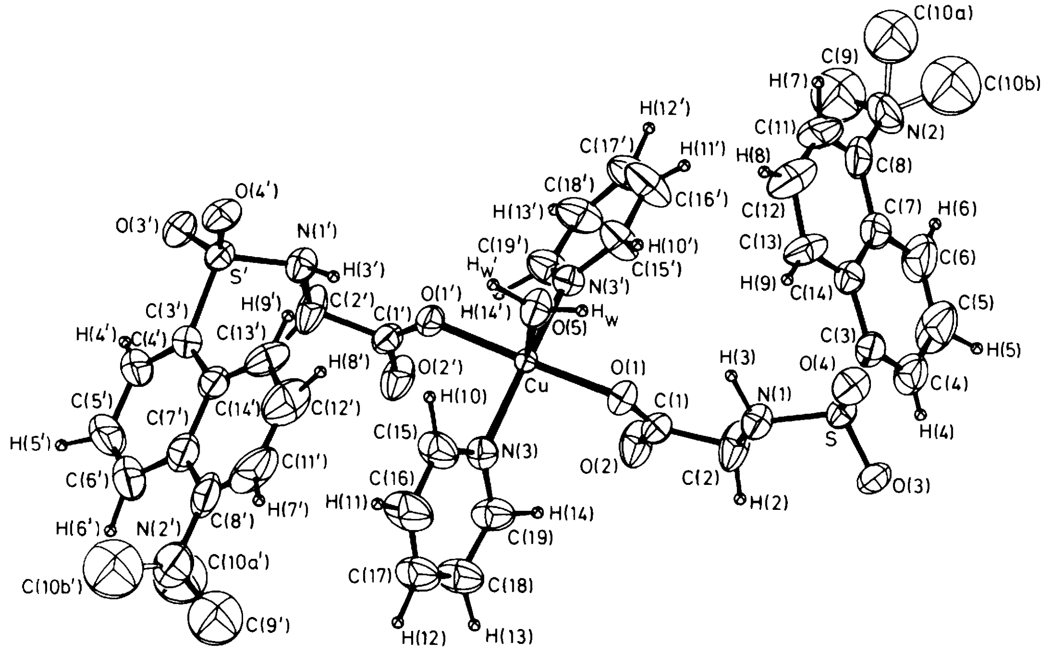


Figure 1. ORTEP view of the $[Cu(dnsglyO)_2(py)_2(H_2O)]$ molecule showing the atom numbering and the thermal motion ellipsoids (40%) for the non-hydrogen atoms. The hydrogen atoms are represented as spheres of arbitrary radius

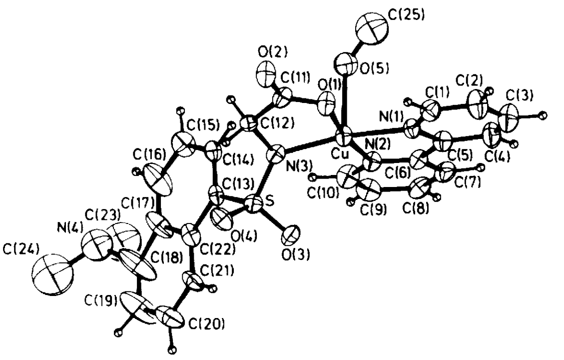


Figure 2. ORTEP view of the $[Cu(dnsglyNO)(bipy)(CH_3OH)]$ molecule showing the atom numbering and the thermal motion ellipsoids (40%) for the non-hydrogen atoms. The hydrogen atoms are represented as spheres of arbitrary radius

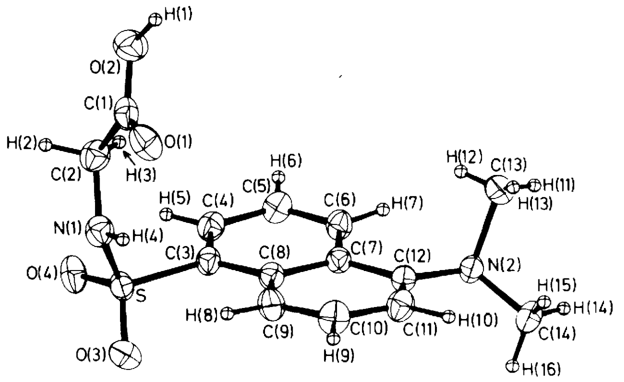


Figure 3. ORTEP view of *N*-dansylglycine showing the atom numbering and the thermal motion ellipsoids (40%) for the non-hydrogen atoms. The hydrogen atoms are represented as spheres of arbitrary radius

5.5, two adducts of formula $[Cu(dnsglyO)_2(py)_2(H_2O)]$ and $[Cu(dnsglyNO)(bipy)(CH_3OH)]$ were obtained in which *N*-dansylglycine shows two different binding modes; in the former adduct the amino-acid molecule is co-ordinated through the carboxylate group, while in the latter it acts in a bidentate manner through the carboxylic oxygen and the deprotonated amide nitrogen atoms. The amide deprotonation observed after the addition of 2,2′-bipyridine to the Cu^{II}–amino-acidate system was not observed with *N*-tosylglycine: the same bipy adduct was only obtained from the reaction of bipy with a binary complex already containing a *N*,*O*-bidentate *N*-tosylglycine molecule co-ordinated to the Cu^{II} ion.[12]

Description of the Structures.—ORTEP views of the pyridine and 2,2′-bipyridine adducts and *N*-dansylglycine are depicted in Figures 1, 2, and 3 respectively. In $[Cu(dnsglyO)_2(py)_2(H_2O)]$ the amino-acid molecule acts as unidentate through the carboxylic oxygen. The copper(II) ion, lying on the two-fold axis, co-ordinates two symmetrically related carboxylic oxygens and two pyridine nitrogens in the basal plane of a tetragonal pyramid, with a water molecule, placed on the same two-fold axis, at the apex [Cu–O(1) 1.954(5), Cu–N(3) 2.04(1), Cu–O(5) 2.196(9) Å]. The basal plane is tetrahedrally distorted, the distances from the mean plane of each atom being 0.113(6) Å for oxygens and −0.183(8) Å for nitrogens; the copper(II) ion is 0.060(2) Å out of this plane toward the water molecule. The sulphonamide nitrogen does not participate in the metal co-ordination and the second carboxylate oxygen O(2) is 3.148(7) Å from the copper(II) ion. Bond distances and angles in the co-ordination polyhedron (Table 6) are similar to those found in ternary complexes of amino acids acting as formally unidentate ligands.[13] The five-co-ordination of this complex is noteworthy since, normally, copper(II)–*N*-protected amino-acidate–pyridine complexes show elongated octahedral co-ordination.[13] In particular, in a complex of *N*-tosylglycine having the same stoicheiometry, the octahedral geometry of the

Table 6. Selected bond distances (Å) and angles (°) for $[Cu(dnsglyO)_2(py)_2(H_2O)]$*

(*a*) In the co-ordination polyhedron

Cu–O(1)	1.954(5)	O(1)–Cu–N(3)	91.1(3)
Cu–N(3)	2.04(1)	O(5)–Cu–N(3)	96.8(3)
Cu–O(5)	2.196(9)	O(5)–Cu–O(1)	88.4(2)
		N(3)–Cu–N(3′)	166.3(3)
		N(3)–Cu–O(1′)	89.3(3)
		O(1)–Cu–O(1′)	176.8(3)

(*b*) In the amino-acid molecule

S–O(3)	1.427(6)	N(1)–S–C(3)	106.5(5)
S–O(4)	1.417(6)	N(1)–S–O(4)	107.2(4)
S–N(1)	1.610(7)	N(1)–S–O(3)	107.0(4)
S–C(3)	1.77(1)	O(4)–S–C(3)	109.6(5)
O(1)–C(1)	1.24(1)	O(3)–S–C(3)	106.8(5)
O(2)–C(1)	1.23(1)	O(3)–S–O(4)	119.0(4)
N(1)–C(2)	1.48(1)	C(2)–N(1)–S	115.7(7)

* Primed atoms are defined by x, y, $\frac{1}{2}-z$.

Table 7. Selected bond distances (Å) and angles (°) for $[Cu(dnsglyNO)(bipy)(CH_3OH)]$

(*a*) In the co-ordination polyhedron

Cu–O(1)	1.97(1)	N(2)–Cu–O(5)	83.4(4)
Cu–N(3)	1.96(1)	N(2)–Cu–N(3)	107.0(5)
Cu–N(1)	1.98(1)	N(2)–Cu–O(1)	169.5(5)
Cu–N(2)	1.96(1)	N(1)–Cu–O(5)	90.3(4)
Cu–O(5)	2.37(1)	N(1)–Cu–N(3)	164.4(4)
		N(1)–Cu–O(1)	90.1(5)
N(3)–Cu–O(5)	103.9(4)	N(1)–Cu–N(2)	80.7(5)
O(1)–Cu–O(5)	91.5(4)		
O(1)–Cu–N(3)	83.2(5)		

(*b*) In the amino-acid molecule

S–O(3)	1.41(1)	N(3)–S–C(13)	108.6(6)
S–O(4)	1.46(1)	N(3)–S–O(4)	109.5(6)
S–N(3)	1.58(1)	N(3)–S–O(3)	108.7(6)
S–C(13)	1.79(1)	O(4)–S–C(13)	106.0(6)
O(1)–C(11)	1.26(2)	O(3)–S–C(13)	109.3(6)
O(2)–C(11)	1.19(2)	O(3)–S–O(4)	114.8(6)
N(3)–C(12)	1.47(2)	C(12)–N(3)–S	117.4(8)

copper(II) ion is reached by formation of a linear-chain water-bridged polymer. In the present complex, the steric hindrance due to the intramolecular contact between the two unco-ordinated carboxylic oxygen atoms placed under the basal co-ordination plane probably prevents the Cu^{II} ion from the activation of the sixth co-ordination position, giving rise to a square-pyramidal environment characterized by a very short Cu–O(water) apical bond. In the amino-acid molecule the C^{α}–COO group is planar, with sulphonamide nitrogen 0.05(1) Å out of this plane, and it forms dihedral angles of 38.7(5) and 102(4)° with the SO_2 and naphthalene group respectively, and 20.7(3)° with the mean plane through the pyridine molecule. The sulphonamide nitrogen atom is involved in a strong intramolecular contact with the unco-ordinated carboxylic oxygen: N(1)···O(2) 2.659(9) Å, N(1)–H(3)···O(2) 92(5)°; furthermore, an intermolecular hydrogen bond occurs between the apical water and the unco-ordinated carboxylic oxygen of the adjacent molecule: O(5)···$O(2^{i})$ 2.707(8) Å, O(5)–H_w···$O(2^{i})$ 174(8)° ($i = \bar{x}, 1 + y, \frac{1}{2} - z$). The packing is determined by van der Waals contacts involving oxygen atoms, dansyl group, and pyridine molecule.

Table 8. Selected bond distances (Å) and angles (°) in the *N*-dansylglycine molecule

S–O(3)	1.425(2)	C(9)–C(10)	1.369(3)
S–O(4)	1.436(2)	C(10)–C(11)	1.411(3)
S–N(1)	1.620(2)	C(11)–C(12)	1.377(3)
S–C(3)	1.789(2)	C(7)–C(12)	1.438(3)
O(1)–C(1)	1.216(3)		
O(2)–C(1)	1.310(3)	N(1)–S–C(3)	107.4(1)
C(1)–C(2)	1.517(3)	O(4)–S–C(3)	106.1(1)
N(1)–C(2)	1.453(3)	O(4)–S–N(1)	107.0(1)
N(2)–C(12)	1.456(3)	O(3)–S–C(3)	109.6(1)
N(2)–C(13)	1.483(3)	O(3)–S–N(1)	107.2(1)
N(2)–C(14)	1.492(3)	O(3)–S–O(4)	119.0(1)
C(3)–C(4)	1.369(3)	S–N(1)–C(2)	118.9(2)
C(4)–C(5)	1.404(3)	C(13)–N(2)–C(14)	108.4(2)
C(5)–C(6)	1.363(3)	C(12)–N(2)–C(14)	114.1(2)
C(6)–C(7)	1.421(3)	C(12)–N(2)–C(13)	112.1(2)
C(7)–C(8)	1.438(3)	O(1)–C(1)–O(2)	125.3(2)
C(3)–C(8)	1.438(3)	O(2)–C(1)–C(2)	113.6(2)
C(8)–C(9)	1.410(3)	O(1)–C(1)–C(2)	121.1(2)

Unlike the above adduct, in $[Cu(dnsglyNO)(bipy)(CH_3OH)]$ the amino-acid molecule acts as bidentate through carboxylic oxygen and deprotonated amide nitrogen atoms, but the co-ordination polyhedron is very similar. Selected bond distances and angles are reported in Table 7. The copper(II) ion exhibits a tetrahedrally distorted square pyramidal N_3O_2 co-ordination arising from ligation of a $dnsglyNO^{2-}$ ion and a bipy molecule in the equatorial plane, and of a methanolic oxygen in the axial position [Cu–O(1) 1.97(1), Cu–N(1) 1.98(1), Cu–N(2) 1.96(1), Cu–N(3) 1.96(1), Cu–O(5) 2.37(1) Å]. The O(3) atom of the SO_2 group is 3.26(1) Å from the copper(II) ion. The four equatorial atoms deviate from the mean plane: N(1) 0.128(9), N(2) −0.18(1), N(3) 0.13(1), O(1) −0.17(1) Å; the copper(II) ion is only 0.108(2) Å out of the mean equatorial plane toward the methanolic oxygen. Another common structural feature is the very small angle between the Cu–O(apical) line and the normal to the mean equatorial plane [7.4(3) and 0° for the bipy and py adduct respectively]. This bipy adduct displays overall structural features nearly identical to those of the structurally known $[Cu(tsglyNO)(bipy)(C_2H_5OH)]$ [tsglyNO = *N*-tosylglycinate(2−)];[12] contrarily to that observed above for the py adduct, the presence of only one *N*-dansylglycine molecule bonded to the copper(II) ion cannot introduce constraints able to modify the co-ordination polyhedron. In the amino-acid molecule the C^{α}–COO group is planar, with the co-ordinated amide nitrogen 0.16(1) Å out of the carboxylate mean plane. This plane is quite orthogonal with SO_2 and the naphthalene group [92.6(7) and 102.7(5)° respectively] and it forms an angle of 16° with the mean bipy plane. The bipy molecule is nearly planar, the two pyridine rings being twisted by 3.5(5)° as usually found.

The *X*-ray crystal structure determination of *N*-dansylglycine was carried out on a crystal obtained after crystallization of the commercial product in aqueous ethanolic (1:2) solution. Selected bond distances and angles are reported in Table 8. The carboxylic group is planar, with the amide nitrogen 0.138(3) Å out of the mean plane, and it forms dihedral angles of 20.1(2) and 106.6(1)° with SO_2 and the naphthalene group respectively. The conformation of the molecule can be described by using torsion angles quoted in Table 9 in which are also reported those found for the amino-acid molecule in the adducts. Clearly, the conformation of the glycine moiety in the free ligand is different from that found in the bipy adduct in which the amino acid exists in the deprotonated form, while it is very similar to that found in the py adduct in which the amino acid is present in its extended form. Torsion angles around the C–C bond of the naphthalene moiety show that this group deviates from planarity in the complexed and uncomplexed amino-acid molecule. An intramolecular contact very similar to that found

Table 9. Selected torsion angles (°) in the amino-acid molecules

N-Dansylglycine		$[Cu(dnsglyO)_2(py)_2(H_2O)]$		$[Cu(dnsglyNO)(bipy)(CH_3OH)]$	
O(1)–C(1)–C(2)–N(1)	−5.0(4)	O(1)–C(1)–C(2)–N(1)	−2(1)	O(1)–C(11)–C(12)–N(3)	6(2)
O(2)–C(1)–C(2)–N(1)	173.9(2)	O(2)–C(1)–C(2)–N(1)	177.7(9)	O(2)–C(11)–C(12)–N(3)	−173(1)
C(1)–C(2)–N(1)–S	−139.4(2)	C(1)–C(2)–N(1)–S	−158.4(8)	C(11)–C(12)–N(3)–S	141.6(9)
O(3)–S–N(1)–C(2)	177.5(2)	O(4)–S–N(1)–C(2)	176.7(8)	O(3)–S–N(3)–C(12)	−154.9(9)
O(4)–S–N(1)–C(2)	−53.8(2)	O(3)–S–N(1)–C(2)	−54.6(9)	O(4)–S–N(3)–C(12)	−27(1)
O(3)–S–C(3)–C(8)	−40.6(3)	O(4)–S–C(3)–C(4)	135.3(9)	O(4)–S–C(13)–C(14)	119(1)
O(4)–S–C(3)–C(8)	−170.2(2)	O(3)–S–C(3)–C(4)	5(1)	O(3)–S–C(13)–C(14)	−116(1)
N(1)–S–C(3)–C(4)	−104.3(2)	N(1)–S–C(3)–C(4)	−109.0(9)	N(3)–S–C(13)–C(14)	2(1)
N(1)–S–C(3)–C(8)	75.6(2)	N(1)–S–C(3)–C(14)	67(1)	N(3)–S–C(13)–C(22)	−179(1)
C(3)–C(8)–C(7)–C(6)	5.6(3)	C(3)–C(14)–C(7)–C(6)	2(2)	C(13)–C(22)–C(17)–C(16)	1(3)
C(3)–C(8)–C(7)–C(12)	−175.9(2)	C(3)–C(14)–C(7)–C(8)	−177(1)	C(13)–C(22)–C(17)–C(18)	173(2)
C(6)–C(7)–C(8)–C(9)	−174.1(2)	C(6)–C(7)–C(14)–C(13)	−179(1)	C(16)–C(22)–C(17)–C(21)	180(2)
C(9)–C(8)–C(7)–C(12)	4.4(4)	C(8)–C(7)–C(14)–C(13)	2(2)	C(18)–C(17)–C(22)–C(2)	−9(3)

in the pyridine adduct is also present in the free ligand [N(1)···O(1) 2.644(3) Å, N(1)–H(4)···O(1) 112(2)°]. A hydrogen bond involving the nitrogen atom of the dimethylamino group O(2)–H(1)···N(2^{i}) $(i = \frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z)$ and van der Waals contacts involving sulphonic oxygen atoms are responsible for the packing. Finally, it is noteworthy that in all the structures reported only C–C contacts between hydrophobic regions of the amino acids are present, without involving intermolecular stacking interactions.

Spectroscopic Investigation of the Adducts.—The electronic spectra of the py adduct (Table 5) are consistent with the presence of the CuN_2O_3 chromophore,[14–16] while the e.s.r. parameters and the electronic spectra of the bipy adduct are very similar to those of the bipy adduct of *N*-tosylglycine[12] as expected from the similarity of their crystal structures. The absorptions in the i.r. spectra of the complexes investigated are assigned to the more significant ligand functions (Table 5).

Conclusions

Though the R group does not influence dramatically the co-ordinative behaviour of $R–SO_2$ amino acids, its steric hindrance may induce some meaningful differences in the co-ordination polyhedra of related compounds (see py adduct). Furthermore, it may influence the number of amino-acid molecules co-ordinated to the copper(II) ion: in fact, unlike that previously observed with *N*-tosylglycine,[12] solid complexes with two copper(II)-bound $dnsglyNO^{2-}$ ions were not separated, even when starting from solutions with a considerable excess of ligand.

The presence of 2,2′-bipyridine has been found to lower the pK_a for the amide nitrogen deprotonation of *N*-dansylglycine interacting with Cu^{II} ion. While the pK_{NH} of *N*-dansylglycine in the presence of Cu^{II} ion has been found to be 8.0 ± 0.2 in water,[2] the separation of the $[Cu(dnsglyNO)(bipy)(CH_3OH)]$ complex has been obtained at pH 5.5. Since this effect was not observed for *N*-tosylglycine, and since 2,2′-bipyridine does not display this effect with small peptide ligands,[1] this argument is somewhat interesting and it requires further investigation. At this stage of the work we may only suggest the favourable effect on the amide deprotonation of *N*-dansylglycine of the presence of a *cis*, strongly copper(II)-co-ordinated ligand such as bipy.

The absence of stacking interactions between the naphthalene groups, but also between the bipy molecules in the bipy adduct, may be due to the great thermal motion of the dimethylamino moiety of the dansyl group.

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