Spectroscopic, Magnetic, and Structural Properties of Diaquadimethanolbis(*N*-tosylvalinato)copper(II) and its 2,2′-Bipyridine Adduct†

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Binary copper(II) compounds of *N*-tosylvalinate (tosyl = toluene-*p*-sulphonyl) of formula $[\{Cu(tsvalO)_2(H_2O)\}_2]\cdot4H_2O$ and $[Cu(tsvalO)_2(H_2O)_2(MeOH)_2]$ were separated. The structure of the latter consists of discrete $[Cu(tsvalO)_2(H_2O)_2(MeOH)_2]$ units in which the copper atom, lying on the symmetry centre, is surrounded by two carboxylic oxygens and two water molecules centrosymmetrically related. Two methanol molecules complete the co-ordination which is elongated tetragonal bipyramidal. The spectroscopic properties are consistent with a CuO_6 chromophore. From its spectroscopic and magnetic properties, a dimeric structure with strong antiferromagnetic exchange ($|2J|$ = 322 cm^{-1}) is inferred for $[\{Cu(tsvalO)_2(H_2O)\}_2]\cdot4H_2O$. The structure of $[\{Cu(tsvalO)_2(bipy)\}_2]$ (bipy = 2,2′-bipyridine) consists of two crystallographically independent dimeric units. In both dimers the co-ordination is distorted tetragonal pyramidal with bipy nitrogens and two carboxylate oxygens of the amino acids in the equatorial plane. In dimer (**I**) the apex of the pyramid is occupied by a bridging carboxylate oxygen which is basal to the centrosymmetric copper atom in the dimer. In dimer (**II**) the two copper atoms are connected by two tosylvalinate ions each bridging *via* an unidentate carboxylate and a sulphonic oxygen. Intermolecular ring-stacking interactions between bipy ligands belonging to two different dimers are present. The large Cu ••• Cu′ separation, Cu–O–Cu′ angle, and the e.s.r. spectra suggest that only very weak exchange interactions may be present.

Use of toluene-*p*-sulphonyl (tosyl, hereafter abbreviated as ts) as a protecting group of amino acids makes the latter very versatile ligands towards copper(II) in comparison to *N*-acetyl, *N*-benzoyl, and *N*-benzyloxycarbonyl amino acids.[1] Simple binary compounds are formed in which the ligand is co-ordinated only through the carboxylic oxygen or through the carboxylic oxygen and deprotonated amide nitrogen atoms.[2] In the last case it is worthy of note that the amide nitrogen deprotonation occurs at pH values (about 5) much lower than those expected for the pK_a (≈ 12) of the amidic group, closely resembling the behaviour of glycine peptide ligands[3,4] and of other similar biologically important systems.[5] In both types of compounds the SO_2 group is sometimes involved in copper(II) co-ordination.[6] Furthermore, the simple compounds easily react with amines to form adducts, which in some cases, present very original structures.[7]

As a part of a systematic investigation into the co-ordinative behaviour of the tosylamino acids toward copper(II), in this paper we report the spectroscopic and magnetic characterization of two simple tosylvalinatocopper(II) compounds and one amine adduct. *X*-Ray structural analyses were also performed for $[Cu(tsvalO)_2(H_2O)_2(MeOH)_2]$ (tsvalO = *N*-tosylvalinate monoanion) and $[\{Cu(tsvalO)_2(bipy)\}_2]$ (bipy = 2,2′-bipyridyl).

Experimental

Preparation of Binary Complexes.—Green $Cu(tsvalO)_2\cdot3H_2O$ was prepared by adding a boiling aqueous solution (100 cm^3) of copper(II) acetate monohydrate (0.1 mol dm^{-3}) to a methanolic solution (50 cm^3) of the amino acid (0.4 mol dm^{-3}). On cooling the solution a green compound precipitated (Found: C, 44.5; H, 5.70; N, 4.40; S, 9.70; H_2O, 8.55. Calc. for $C_{24}H_{38}CuN_2O_{11}S_2$: C, 43.75; H, 5.80; N, 4.25; S, 9.75; H_2O, 8.20%).

Pale blue diaquadimethanolbis(*N*-tosylvalinato)copper(II), $[Cu(tsvalO)_2(H_2O)_2(MeOH)_2]$, precipitated after several weeks upon evaporation of the solution from which the green compound had been filtered off (Found: C, 44.2; H, 6.25; N, 4.00; S, 8.95;. Calc. for $C_{26}H_{44}CuN_2O_{12}S_2$: C, 44.2; H, 6.30; N, 4.00; S, 9.1%).

Preparation of the Dimeric Ternary Complex $[\{Cu(tsvalO)_2(bipy)\}_2]$.—Deep blue crystals were separated from an alcoholic (EtOH : MeOH = 1 : 1) solution of the green or blue compound (0.01 mol dm^{-3}) containing a slight excess of 2,2′-bipyridine (0.015 mol dm^{-3}) (Found: C, 53.0; H, 5.46; N, 7.35; S, 8.30. Calc. for $C_{68}H_{80}Cu_2N_8O_{16}S_4$: C, 53.7; H, 5.30; N, 7.35; S, 8.45%).

Physical Measurements.—Diffuse reflectance spectra were recorded with a Varian-Cary 2300 spectrophotometer, i.r. spectra with a Perkin-Elmer 521 spectrophotometer as KBr pellets and as Nujol mulls on KBr as support in the range 4 000—250 cm^{-1}. 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 calibrating field marker. Magnetic susceptibility measurements were made on a Newport Instruments magnetic (Gouy) balance employing a cryostatic cooling system, with $Hg[Co(SCN)_4]$ as calibrant, and were corrected for diamagnetism $\{-334.42 \times 10^{-12}$ and -403.46×10^{-12} m^3 mol^{-1} for $Cu(tsvalO)_2\cdot3H_2O$ and $[\{Cu(tsvalO)_2(bipy)\}_2]$ respectively$\}$ with the appropriate Pascal constants. Thermogravimetric analyses were performed at a heating rate of 5 °C min^{-1} with a Mettler TA 3000 instrument.

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† *Supplementary data available* (No. SUP 56662, 4 pp.): molar susceptibilities, magnetic moments. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.

Table 1. Summary of crystal data collection *

	$[Cu(tsvalO)_2(H_2O)_2(MeOH)_2]$	$[\{Cu(tsvalO)_2(bipy)\}_2]$
Formula	$C_{26}H_{44}CuN_2O_{12}S_2$	$C_{68}H_{80}Cu_2N_8O_{16}S_4$
M	704.3	1 520.8
Crystal system	Monoclinic	Triclinic
a/Å	4.996(2)	16.864(4)
b/Å	19.304(7)	16.075(4)
c/Å	17.124(6)	13.783(3)
α/°	90	75.6(1)
β/°	97.93(1)	73.4(1)
γ/°	90	85.8(1)
U/Å^3	1 636(1)	3 468(3)
Space group	$P2_1/n$	$P\bar{1}$
D_c/g cm^{-3}	1.43	1.46
D_m/g cm^{-3}	1.41 (by flotation)	1.44 (by flotation)
$F(000)$	742	1 588
Reflections measured	$\pm h, +k, +l$	$\pm h, \pm k, +l$
Scan width/°	$1.5 + 0.35 \tan\theta$	$1.2 + 0.35 \tan\theta$
Collected reflections	2 974	9 660
Observed reflections	2 268 $[I > 3\sigma(I)]$	4 215 $[I > 2\sigma(I)]$
Independent reflections	2 192	4 204
Crystal size/mm	$0.20 \times 0.22 \times 0.35$	$0.26 \times 0.52 \times 0.55$
μ/cm^{-1}	26.11	24.4

* Common to both complexes: $Z = 2$; nickel-filtered Cu-K_α radiation ($\lambda = 1.541\,78$ Å); scan type ω—2θ; θ range 3—65°; lowest scan speed 2.5° min^{-1}; standard reflections, 1 every 50 (no change).

X-Ray Data Collection and Structure Determination.—For both compounds, diffraction data were obtained by mounting a crystal with the c axis coincident with the φ axis of a Siemens AED single-crystal automated diffractometer. Unit-cell dimensions were determined by least-squares refinement of the best angular positions for 15 high-angle reflections ($\theta > 60°$) for $[Cu(tsvalO)_2(H_2O)_2(MeOH)_2]$ and for 20 reflections for $[\{Cu(tsvalO)_2(bipy)\}_2]$. Crystal data and structural details are reported in Table 1. For both complexes the intensity data were corrected for Lorentz and polarization effects, but not for absorption. For $[Cu(tsvalO)(H_2O)_2(MeOH)_2]$ the μr value is very low (0.27) and the absorption coefficient, A^*, practically invariant (1.56—1.53) over the range θ 3—65° assuming a cylindrical shape for the crystal; for $[\{Cu(tsvalO)_2(bipy)\}_2]$ ($\mu r = 0.63$, $A^* = 2.83$—2.46 in the same θ range), the irregular nature of the crystal precluded absorption correction because of difficulties in measuring the specimen shape.

The structures were solved by the heavy-atom technique and refined by least squares. The function minimized in the refinement was $\Sigma w|\Delta F|^2$, using the weighting scheme $w = k/[\sigma^2(F_o) + gF_o^2]$. Residual R and R' indices are defined as $R = \Sigma|\Delta F|/|F_o|$ and $R' = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{\frac{1}{2}}$. The structure of $[Cu(tsvalO)_2(H_2O)_2(MeOH)_2]$ was refined by several full-matrix least-squares cycles, first isotropically, then anisotropically to convergence at $R = 0.07$. At this stage the ΔF map revealed all the hydrogen atoms, which were introduced as fixed contributors in the final refinement. Twelve reflections probably affected by extinction or counting errors were excluded from the refinement. In the final refinement the R factor was 0.055 $\{R' = 0.064$ using the weighting scheme $w = 1.28/[\sigma^2(F_o) + 0.036\, F_o^2]\}$. The refinement of the structure of $[\{Cu(tsvalO)_2(bipy)\}_2]$ was carried out anisotropically for Cu, S, O, and N atoms and for bipyridine molecules, isotropically for the other carbon atoms, by several blocked-matrix least-squares cycles. The R index was 0.072 $\{R' = 0.078$ using the weighting scheme $w = 0.5653/[\sigma^2(F_o) + 0.011\,029\, F_o^2]\}$.

The final positional parameters are in Tables 2 and 3; neutral atom scattering factors were used with anomalous dispersion corrections applied to all non-hydrogen atoms.[8] Major calculations were performed on a CDC 7600 computer by using the SHELX 76 system of programs.[9]

Table 2. Fractional atomic co-ordinates ($\times 10^4$) of $[Cu(tsvalO)_2(H_2O)_2(MeOH)_2]$

Atom	X/a	Y/b	Z/c
Cu	5 000	5 000	5 000
S	3 729(2)	2 995(1)	7 844(1)
O(1)	3 655(7)	4 642(2)	5 940(2)
O(2)	7 489(7)	4 135(2)	6 474(2)
O(3)	5 207(8)	2 629(2)	8 490(2)
O(4)	960(7)	3 160(2)	7 866(2)
O(5)	1 769(7)	4 603(2)	4 343(2)
O(6)	7 794(8)	3 938(2)	4 931(2)
N	5 298(8)	3 717(2)	7 762(2)
C(1)	5 191(9)	4 349(2)	6 511(3)
C(2)	4 041(9)	4 299(2)	7 291(3)
C(3)	4 564(12)	4 973(3)	7 778(3)
C(4)	3 466(15)	5 615(3)	7 337(4)
C(5)	3 379(17)	4 916(4)	8 549(4)
C(6)	3 890(11)	2 496(3)	6 984(3)
C(7)	5 863(12)	2 011(3)	6 983(4)
C(8)	6 069(14)	1 629(3)	6 299(4)
C(9)	4 199(14)	1 721(3)	5 625(4)
C(10)	4 484(22)	1 309(5)	4 901(5)
C(11)	2 229(14)	2 207(4)	5 645(4)
C(12)	2 011(13)	2 605(4)	6 313(4)
C(13)	6 328(23)	3 313(5)	4 555(7)

Analyses.—Sulphur, nitrogen, carbon, and hydrogen were analysed with a C. Erba model 1106 elemental analyser by Mr. G. Pistoni. The water content was determined gravimetrically.

Results and Discussion

From aqueous methanol (1 : 1) solution two simple binary compounds were separated, one green of formula $Cu(tsvalO)_2 \cdot 3H_2O$ and one pale blue of formula $[Cu(tsvalO)_2(H_2O)_2(MeOH)_2]$. For the green compound, magnetic (in the range 120—302 K) and spectroscopic properties in the solid state and in methanol solution (Table 4) are suggestive of a binuclear species with strong antiferromagnetic exchange.[2] In particular, the $2J$ value, calculated in the usual manner,[2,10] closely agrees with those found for copper(II) dimers of other N-protected amino acids (273—351 cm^{-1})[2] and carboxylic acids (275—340 cm^{-1});[11,12] it indicates an interaction *via* a superexchange mechanism and a structure similar to that of copper acetate. Furthermore, the presence of co-ordinated and unco-ordinated water molecules (see i.r. spectrum), both lost in the range 313—433 K, and the absence of splitting of the i.r. bands of the sulphonic group enable us to suggest for this compound the presence of discrete dimeric units of formula $[\{Cu(tsvalO)_2(H_2O)\}_2] \cdot 4H_2O$.

For the pale blue compound the crystal and molecular structure was determined.

Description of the Structure of $[Cu(tsvalO)_2(H_2O)_2(MeOH)_2]$. —The structure of the complex (Figure 1) consists of discrete $[Cu(tsvalO)_2(H_2O)_2(MeOH)_2]$ units, in which the copper atom, lying on the centre of symmetry, is surrounded by two carboxylic oxygens [Cu–O(1) 1.954(4) Å] and two water molecules [Cu–O(5) 1.989(3) Å] related by the symmetry centre. Two methanol molecules complete the co-ordination to elongated tetragonal bipyramid [Cu–O(6) 2.492(4) Å]. The equatorial atoms are coplanar according to the symmetry requirement, the distortion of the co-ordination polyhedron

Table 3. Fractional atomic co-ordinates (× 10^4) of [{Cu(tsvalO)$_2$(bipy)}$_2$]

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	625(1)	914(1)	4 438(1)	C(68)	4 312(7)	1 282(8)	3 271(9)
S(1)	−527(2)	4 548(2)	3 828(3)	C(1)	−100(6)	2 386(7)	5 046(8)
S(2)	1 367(3)	−1 542(3)	8 581(3)	C(2)	−837(7)	2 978(7)	5 198(9)
O(1)	−247(4)	1 683(4)	4 841(6)	C(3)	−1 358(7)	2 709(7)	6 357(9)
O(2)	587(4)	2 575(5)	5 079(6)	C(4)	−949(8)	2 845(9)	7 151(11)
O(3)	−479(6)	4 077(5)	3 087(7)	C(5)	−2 160(10)	3 246(11)	6 420(13)
O(4)	95(5)	5 155(5)	3 677(7)	C(6)	−1 459(7)	5 113(7)	3 944(9)
O(5)	298(4)	77(4)	5 809(5)	C(7)	−2 103(9)	4 795(9)	3 732(11)
O(6)	1 306(5)	536(5)	6 253(6)	C(8)	−2 871(9)	5 223(10)	3 882(12)
O(7)	762(6)	−2 174(7)	8 825(9)	C(9)	−2 957(8)	5 976(8)	4 164(10)
O(8)	1 732(7)	−1 413(9)	9 359(8)	C(10)	−3 763(10)	6 507(10)	4 281(12)
N(1)	−557(6)	3 888(6)	4 933(8)	C(11)	−2 285(8)	6 320(9)	4 308(11)
N(2)	981(6)	−591(6)	8 133(8)	C(12)	−1 532(7)	5 895(8)	4 219(9)
N(3)	1 068(5)	1 746(6)	3 020(7)	C(13)	700(5)	84(6)	6 469(7)
N(4)	1 616(5)	273(6)	3 897(7)	C(14)	389(6)	−518(7)	7 518(8)
C(25)	694(8)	2 461(7)	2 638(9)	C(15)	−436(7)	−175(7)	8 143(9)
C(26)	1 101(8)	3 061(8)	1 684(10)	C(16)	−797(8)	−833(8)	9 201(10)
C(27)	1 901(9)	2 867(8)	1 159(9)	C(17)	−357(8)	705(9)	8 288(10)
C(28)	2 274(7)	2 100(8)	1 568(9)	C(18)	2 155(7)	−1 727(8)	7 532(10)
C(29)	1 842(7)	1 542(7)	2 478(8)	C(19)	2 075(8)	−2 395(9)	7 075(11)
C(30)	2 147(6)	706(7)	2 983(9)	C(20)	2 771(10)	−2 568(10)	6 295(12)
C(31)	2 919(7)	357(9)	2 539(10)	C(21)	3 503(10)	−2 086(11)	5 970(13)
C(32)	3 128(7)	−453(10)	3 043(11)	C(22)	4 233(11)	−2 283(12)	5 097(14)
C(33)	2 594(7)	−900(8)	3 948(10)	C(23)	3 555(10)	−1 452(11)	6 466(13)
C(34)	1 857(7)	−526(7)	4 357(9)	C(24)	2 873(9)	−1 262(9)	7 243(11)
Cu(2)	4 419(1)	2 833(1)	1 471(1)	C(35)	5 118(6)	1 340(7)	697(8)
S(3)	5 619(2)	−741(2)	2 224(3)	C(36)	5 849(7)	740(7)	693(8)
S(4)	4 208(2)	5 933(2)	−2 126(3)	C(37)	6 457(7)	869(8)	−416(8)
O(9)	5 224(5)	1 998(5)	1 024(6)	C(38)	7 169(8)	236(8)	−413(10)
O(10)	4 527(5)	1 203(5)	464(7)	C(39)	6 783(9)	1 808(9)	−745(11)
O(11)	5 657(6)	−216(6)	2 879(8)	C(40)	6 566(7)	−1 305(7)	2 065(9)
O(12)	4 971(6)	−1 371(7)	2 519(9)	C(41)	6 654(7)	−1 943(8)	1 492(9)
O(13)	3 803(5)	3 266(5)	−245(7)	C(42)	7 359(7)	−2 388(8)	1 387(9)
O(14)	4 824(4)	3 758(5)	177(5)	C(43)	8 015(8)	−2 228(8)	1 724(10)
O(15)	4 149(5)	5 747(6)	−3 034(7)	C(44)	8 816(9)	−2 765(10)	1 576(12)
O(16)	4 593(5)	6 724(6)	−2 206(7)	C(45)	7 908(8)	−1 613(8)	2 291(10)
N(5)	5 574(6)	−170(7)	1 085(9)	C(46)	7 185(8)	−1 135(8)	2 450(10)
N(6)	4 736(6)	5 203(6)	−1 536(8)	C(47)	4 411(6)	3 720(7)	−476(9)
N(7)	3 961(6)	2 025(6)	2 873(7)	C(48)	4 701(7)	4 309(8)	−1 570(9)
N(8)	3 438(8)	3 549(6)	2 048(7)	C(49)	5 559(7)	4 005(8)	−2 144(9)
C(59)	3 248(8)	4 349(7)	1 558(10)	C(50)	5 895(9)	4 628(9)	−3 208(11)
C(60)	2 540(8)	4 762(9)	1 987(11)	C(51)	5 434(8)	3 071(9)	−2 230(11)
C(61)	1 994(7)	4 278(10)	2 933(11)	C(52)	3 196(7)	5 911(8)	−1 301(9)
C(62)	2 183(6)	3 458(8)	3 404(9)	C(53)	2 974(8)	6 503(8)	−691(10)
C(63)	2 935(7)	3 115(7)	2 944(9)	C(54)	2 157(8)	6 495(9)	−69(11)
C(64)	3 216(6)	2 269(7)	3 439(9)	C(55)	1 608(8)	5 911(9)	−82(10)
C(65)	2 784(8)	1 742(8)	4 411(9)	C(56)	702(10)	5 859(11)	607(13)
C(66)	3 154(7)	969(8)	4 798(9)	C(57)	1 832(10)	5 294(10)	−675(12)
C(67)	3 934(8)	738(8)	4 248(10)	C(58)	2 686(9)	5 281(9)	−1 319(11)

being measured by considering the angle between the line Cu–O(6) and the normal to the equatorial plane [4.2(1)°].

The amide nitrogen and the second carboxylic oxygen are not involved in the co-ordination, the amino acid acting as a simple unidentate carboxylate. The distance of the non-bonded second carboxylic oxygen O(2) from the copper is 3.137(4) Å. The C^{α}–CO_2^- group is planar, with the nitrogen atom 0.600(4) Å out of this plane, and forms dihedral angles of 53.3(2)° with the sulphonic group and 139.7(2)° with the phenyl ring. Bond distances and angles (Table 5) are in the range of those found in other *N*-tosylamino acid complexes,[2] and the C–O distances for the co-ordinated and unco-ordinated carboxylic oxygens are in agreement with those of unidentate carboxylate complexes. The packing is determined by inter- and intra-molecular hydrogen bonds involving amide nitrogen, water, methanolic oxygen atoms, and co-ordinated and unco-ordinated carboxylic oxygens.

Indistinguishable water and methanol molecules are lost in the range 310—425 K. The 'rhombic type' e.s.r. spectrum of the compound (Table 4) is consistent with the differences in equatorial Cu–O distances. The *d*–*d* band maximum (Table 4) has an energy typical of compounds having a CuO_6 chromophore.[13]

Both the green and blue compounds readily react with amines, forming ternary complexes which contain a combination of donor atoms, such as heteroatomic N base moieties and O donors, which are recognized as enhancing the stability of such complexes.[14] A great number of ternary complexes of copper and N-protected amino acids have been reported (see references in ref. 2). For this reason we describe only the results obtained for [{Cu(tsvalO)$_2$(bipy)}$_2$] which itself exhibits peculiar characteristics.

Description of the Structure of [{Cu(tsvalO)$_2$(bipy)}$_2$].—

Table 4. Room-temperature (298 K) electronic, i.r., e.s.r., and magnetic moments, low-temperature e.s.r. and magnetic moments, weight-loss temperature range, and decomposition temperature for copper(II) *N*-tosylvalinates

	$[\{Cu(tsvalO)_2(H_2O)\}_2]\cdot 4H_2O$	$[Cu(tsvalO)_2(H_2O)_2(MeOH)_2]$	$[\{Cu(tsvalO)_2(bipy)\}_2]$
Wt. loss temp. range/K	313—433	310—425	
Decomp. temp./K	438	433	
$\mu_{eff.}$ (298 K)	1.43	1.85	1.84
$\mu_{eff.}$(low temp.)	0.62 (at 124 K)		1.86 (at 102.5 K)
d–*d* Band, $\nu/10^3$ cm^{-1}	13.5 ^{a}	13.2	15.6, 14.5br
$g_{\parallel}$	2.41,^{b} 2.42^c	$g_3 = 2.401$	2.295
$g_{\perp}$	2.10, 2.12	$g_2 = 2.110, g_1 = 2.069$	2.070
$\langle g \rangle^d$	2.20, 2.22^e	2.193	2.145
ν(OH)/cm^{-1}	3 530br, 3 460s	3 600, 3 400mbr	
ν(NH)/cm^{-1}	3 320ms, 3 280m	3 250s	3 320s
ν_{asym}(OCO)/cm^{-1}	1 640	1 630vs	1 635, 1 595vs
ν_{sym}(OCO)/cm^{-1}	1 400	1 380vs	1 365vs
$\nu_{asym}(SO_2)$/cm^{-1}	1 325	1 315vs	1 345, 1 315vs
$\nu_{sym}(SO_2)$/cm^{-1}	1 160	1 150vs	1 150vs

[a] Charge-transfer band at 26 700 (sh) cm^{-1}. [b] For monomer: $g_{\parallel} = 2.365, g_{\perp} = 2.200, A_{\parallel} = 155 \times 10^{-4}$ cm^{-1}. [c] Frozen methanolic saturated solution. [d] $\langle g \rangle = [(g_{\parallel} + 2g_{\perp})/3]$. [e] *D* (zero field splitting parameter) = 0.38 cm^{-1}, $|2J| = 322 \pm 1$ cm^{-1}.

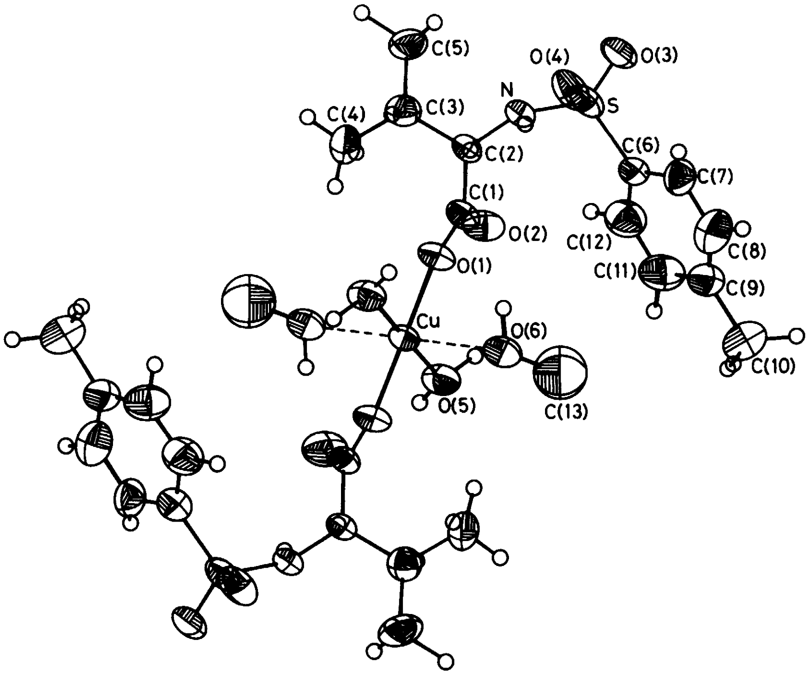

Figure 1. ORTEP view of $[Cu(tsvalO)_2(H_2O)_2(MeOH)_2]$

Bond distances and angles are reported in Table 6. The structure consists of two discrete crystallographically independent dimeric units, in which the amino acid molecules exhibit different co-ordinative behaviour.

In the dimer (**I**) (Figure 2) each copper atom co-ordinates one bipy and two amino acid molecules, acting in a unidentate manner through one carboxylic oxygen atom. The copper atoms are connected by an asymmetric bridge through two carboxylic oxygens related by an inversion centre in the middle of the dimer. The co-ordination around each copper atom is distorted tetragonal pyramidal, with the bipy nitrogens and carboxylate oxygens [Cu–N 2.044(9), 1.967(9); Cu–O 1.899(7), 1.983(6) Å] in the equatorial plane and the axial position occupied by a bridging carboxylate oxygen [Cu–O 2.452(8) Å], which is basal to the centrosymmetric copper atom in the dimer.

In the dimer (**II**), Figure 3, two centrosymmetrically related copper atoms are present, linked by one tosylvalinate molecule, which is bidentate through one carboxylic oxygen and one sulphonic oxygen atom. The co-ordination around each copper involves one bipy molecule [Cu–N 2.016(8), 2.029(9) Å] and two carboxylic oxygens [Cu–O 1.921(8), 1.998(7) Å] belonging to two different *N*-tosylvaline molecules in the equatorial plane of a square pyramid with one sulphonic oxygen at the apex [Cu–O 2.410(11) Å]. In this way the two copper atoms in the dimer are connected by two tosylvalinate ions *via* the unidentate carboxylate and sulphonic groups.

In the co-ordination polyhedra the equatorial planes are tetrahedrally distorted, with atomic deviations from −0.015 to 0.015 Å for dimer (**I**) and from −0.107 to 0.079 Å for dimer (**II**). The copper atoms lie out of the plane by 0.06 Å for (**I**) and 0.017

Å for (II) towards the apical oxygen atoms, the angles between the apical bonds and the normal to the mean planes of the co-ordination polyhedra being 15.2(3) and 5.9(3)° for (I) and (II) respectively.

The arrangement of amino acids in dimer (I) with metal atoms bridged by unidentate carboxylate groups is similar to that found in [{Cu(tsglyO)$_2$(bipy)}$_2$]·2H$_2$O[7] (tsglyO = *N*-tosylglycinate monoanion), where very similar bond distances were found [Cu ··· Cu′ 3.501(5) Å and bridged Cu–O–Cu angle 103.7(4)° in the present compound; 3.317(1) Å and 100.0(1)° in the tosylglycine derivative].

In the dimer (II) the sulphonic oxygen atom is co-ordinated to the metal [Cu–O 2.410(11) Å]. This has been found only in a few complexes of copper(II), giving rise in all cases to dimeric or polymeric structures. In K$_2$[Cu(tsglyNO)$_2$][15] (tsglyNO = *N*-tosylglycinate dianion) the sulphonic group is involved in a weak interaction [Cu–O 2.717(3) Å] forming dimeric units and in [{Cu(tsglyO)$_2$}$_n$][6] it links *via* Cu–O(SO$_2$) bonds [2.168(7) Å] the dimeric copper(II) tosylglycinate molecules, forming polymeric chains. In the present compound two symmetry-related tosylvalinate ions, in the extended form, connect two copper atoms [Cu(2) ··· Cu(2′) (1 − *x*, 1 − *y*, −*z*) 7.226(5) Å] through one sulphonic and one carboxylate oxygen atom.

Though it is known that the ligand field of in-plane donors affects the axial interactions, in the present complexes no correlation was found between the variation in the axial bond lengths and the nature of the equatorial ligands. It seems more probable that the steric hindrance of the ligand is responsible for these large variations.

The bond distances and angles in the independent amino acid molecules are similar and consistent with those observed in other *N*-protected amino acid complexes of Cu^{II}.[2] In the bipy molecules, the pyridine rings are planar and twisted around the

Table 5. Bond distances (Å) and angles (°) for [Cu(tsvalO)$_2$(H$_2$O)$_2$(MeOH)$_2$]

(*a*) In the co-ordination polyhedron			
Cu–O(1)	1.954(4)	O(5)–Cu–O(6)	94.1(1)
Cu–O(5)	1.989(3)	O(1)–Cu–O(6)	90.4(1)
Cu–O(6)	2.492(4)	O(1)–Cu–O(5)	89.1(1)
(*b*) In the ligand molecule			
S–O(3)	1.429(4)	C(3)–C(4)	1.514(8)
S–O(4)	1.425(4)	C(3)–C(5)	1.524(9)
S–N	1.615(4)	C(6)–C(7)	1.360(8)
S–C(6)	1.771(6)	C(6)–C(12)	1.396(8)
O(1)–C(1)	1.288(6)	C(7)–C(8)	1.400(9)
O(2)–C(1)	1.230(6)	C(8)–C(9)	1.392(9)
O(6)–C(13)	1.509(11)	C(9)–C(10)	1.496(11)
N–C(2)	1.472(6)	C(9)–C(11)	1.364(10)
C(1)–C(2)	1.528(7)	C(11)–C(12)	1.394(10)
C(2)–C(3)	1.548(7)		
N–S–C(6)	108.6(2)	N–C(2)–C(3)	108.6(4)
O(4)–S–C(6)	107.4(2)	C(2)–C(3)–C(5)	110.4(5)
O(4)–S–N	107.1(2)	C(2)–C(3)–C(4)	113.4(5)
O(3)–S–C(6)	107.3(2)	C(4)–C(3)–C(5)	109.5(5)
O(3)–S–N	106.8(2)	S–C(6)–C(12)	120.0(5)
O(3)–S–O(4)	119.3(2)	S–C(6)–C(7)	119.5(4)
Cu–O(1)–C(1)	123.0(3)	C(7)–C(6)–C(12)	120.5(6)
Cu–O(6)–C(13)	115.8(5)	C(6)–C(7)–C(8)	120.0(6)
S–N–C(2)	112.0(3)	C(7)–C(8)–C(9)	120.5(6)
O(1)–C(1)–O(2)	124.8(5)	C(8)–C(9)–C(11)	118.1(6)
O(2)–C(1)–C(2)	119.3(4)	C(8)–C(9)–C(10)	119.3(7)
O(1)–C(1)–C(2)	115.8(4)	C(10)–C(9)–C(11)	122.6(7)
N–C(2)–C(1)	110.1(3)	C(9)–C(11)–C(12)	122.5(7)
C(1)–C(2)–C(3)	111.2(4)	C(6)–C(12)–C(11)	118.2(6)

Table 6. Selected bond distances (Å) and angles (°) for [{Cu(tsvalO)$_2$(bipy)}$_2$]

Dimer (I)[a]				Dimer (II)[b]			
(*a*) In the co-ordination polyhedra							
Cu(1)–O(1)	1.899(7)	N(3)–Cu(1)–N(4)	81.4(5)	Cu(2)–O(9)	1.921(8)	N(1)–Cu(2)–N(8)	81.3(5)
Cu(1)–O(5)	1.983(6)	N(4)–Cu(1)–O(5′)	92.8(5)	Cu(2)–O(14)	1.998(7)	N(8)–Cu(2)–O(16′)	98.8(4)
Cu(1)–N(3)	2.044(9)	N(3)–Cu(1)–O(5′)	106.3(4)	Cu(2)–N(7)	2.016(8)	N(7)–Cu(2)–O(16′)	87.0(4)
Cu(1)–N(4)	1.967(9)	O(5)–Cu(1)–N(3)	174.9(7)	Cu(2)–N(8)	2.029(9)	N(8)–Cu(2)–O(14)	92.5(4)
Cu(1)–O(5′)	2.452(8)	O(5)–Cu(1)–O(5′)	76.2(4)	Cu(2)–O(16′)	2.410(11)	N(7)–Cu(2)–O(14)	172.5(5)
		O(1)–Cu(1)–N(4)	171.6(5)			O(14)–Cu(2)–O(16′)	89.8(4)
		O(1)–Cu(1)–N(3)	91.3(5)			O(9)–Cu(2)–N(7)	91.6(5)
		O(1)–Cu(1)–O(5′)	93.3(5)			O(9)–Cu(2)–O(16′)	87.0(5)
		O(1)–Cu(1)–O(5)	92.6(4)			O(9)–Cu(2)–O(14)	95.0(4)
(*b*) In the ligand molecules							
S(1)–O(3)	1.397(11)	S(2)–O(7)	1.40(1)	S(3)–O(11)	1.40(1)	S(4)–O(15)	1.39(1)
S(1)–O(4)	1.421(9)	S(2)–O(8)	1.44(1)	S(3)–O(12)	1.44(1)	S(4)–O(16)	1.44(1)
S(1)–N(1)	1.61(1)	S(2)–N(2)	1.66(1)	S(3)–N(5)	1.63(1)	S(4)–N(6)	1.62(1)
S(1)–C(6)	1.74(1)	S(2)–C(18)	1.73(1)	S(3)–C(40)	1.39(1)	S(4)–C(52)	1.76(1)
O(1)–C(1)	1.29(1)	O(5)–C(13)	1.28(1)	O(9)–C(35)	1.29(1)	O(14)–C(47)	1.30(1)
O(2)–C(1)	1.23(1)	O(6)–C(13)	1.22(1)	O(10)–C(35)	1.18(1)	O(13)–C(47)	1.22(1)
N(1)–C(2)	1.49(1)	N(2)–C(14)	1.46(2)	N(5)–C(36)	1.49(1)	N(6)–C(48)	1.46(2)
N(1)–S(1)–C(6)	108.8(7)	N(2)–S(2)–C(8)	104.8(7)	N(5)–S(3)–C(40)	108.4(6)	N(6)–S(4)–C(52)	107.5(6)
O(4)–S(1)–C(6)	106.5(8)	O(8)–S(2)–C(18)	108.4(8)	O(12)–S(3)–C(40)	107.0(8)	O(16)–S(4)–C(52)	108.8(7)
O(4)–S(1)–N(1)	105.3(7)	O(8)–S(2)–N(2)	105.0(8)	O(12)–S(3)–N(5)	104.3(8)	O(16)–S(4)–N(6)	104.1(8)
O(3)–S(1)–C(6)	106.3(8)	O(7)–S(2)–C(18)	107.4(8)	O(11)–S(3)–C(40)	104.3(8)	O(15)–S(4)–C(52)	106.7(8)
O(3)–S(1)–N(1)	108.8(7)	O(7)–S(2)–N(2)	109.0(9)	O(11)–S(3)–N(5)	111.1(8)	O(15)–S(4)–N(6)	111.0(7)
O(3)–S(1)–O(4)	120.7(7)	O(7)–S(2)–O(8)	121.1(8)	O(11)–S(3)–O(12)	121.2(8)	O(15)–S(4)–O(16)	118.4(7)
Cu(1)–O(1)–C(1)	120.8(9)	Cu(1)–O(5)–C(13)	117.8(7)	Cu(2)–O(9)–C(35)	128.3(10)	Cu(2)–O(14)–C(47)	108.7(8)
S(1)–N(1)–C(2)	123.0(9)	S(2)–N(2)–C(14)	120.5(9)	S(3)–N(5)–C(36)	122.1(10)	S(4)–N(6)–C(48)	121.0(10)

[a] Primed atoms at $\bar{x},\bar{y},1 - z$. [b] Primed atoms at $1 - x,1 - y,\bar{z}$.

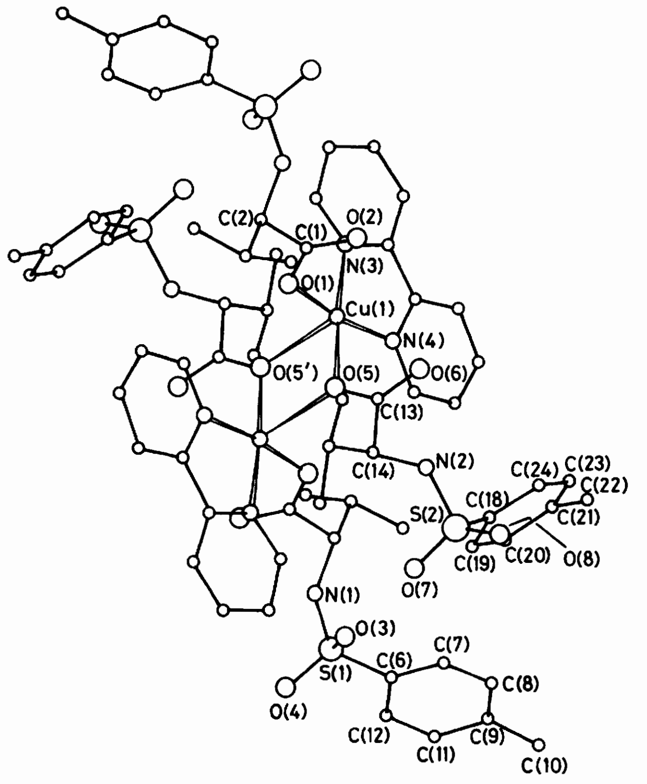

Figure 2. Clinographic projection of $[\{Cu(tsvalO)_2(bipy)\}_2]$, dimer (I)

2,2′ bond, by 5.0(3)° in dimer (I) and 6.5(4)° in dimer (II). These values are in the range of those found in other bipy complexes.[7]

The dimers of type (I) are connected along the [010] axis by contacts involving amide nitrogen and sulphonic oxygen atoms $[N(1)\cdots O(4^{I})$ $(-x, 1-y, 1-z)$ 3.02(2) Å], the dimers (II) by $N(5)\cdots O(10^{II})$ $(1-x, -y, -z)$ 3.06(2), $N(6)\cdots O(14^{III})$ $(1-x, 1-y, -z)$ 3.06(1) Å which can be considered as hydrogen bonds. Intermolcular ring-stacking interactions between bipyridine ligands belonging to two different dimers are present, as found in other complexes.[16]

The physical properties of the compound (Table 4) must be considered averaged values, since the environments around each copper(II) ion in the two dimers are too similar to distinguish the contribution arising from each dimeric unit.

Magnetic susceptibility measurements of polycrystalline samples between 102 and 308 K strictly obey the Curie–Weiss law with constants $C = 0.237\ T^2J^{-1}\ K^{-1}\ mol^{-1}$, $\theta = -2.2$ K, and $g = 2.12$ in agreement with the average value of g 2.14 obtained from e.s.r. spectra (Table 4). The e.s.r. spectra at different temperatures, which are very similar, are of axial type with g values consistent with the CuN_2O_3 chromophore. At 139 K a low-field resonance corresponding to $\Delta M = 2$ is present, indicating magnetically coupled copper(II) ions probably corresponding to dimer (I), but the very good agreement of the magnetic data with the Curie–Weiss law down to 102 K suggests that only very weak exchange interactions may be present. This result, in agreement with the reported values for structurally analogous compounds,[7,17] is attributed to the quasi-orthogonality between the s and p orbitals on the bridging oxygen and the orbital on one copper that contains unpaired spin [Cu–O–Cu 103.7(4)° in the present compound, 100.0(1)° in $[\{Cu(tsglyO)_2(bipy)\}_2]\cdot 2H_2O$,[7] and 101.0° in $[\{Cu(bzglyO)_2(H_2O)_4\}_2]$[18] (bzglyO = *N*-benzoylglycinate or hippurate anion)].

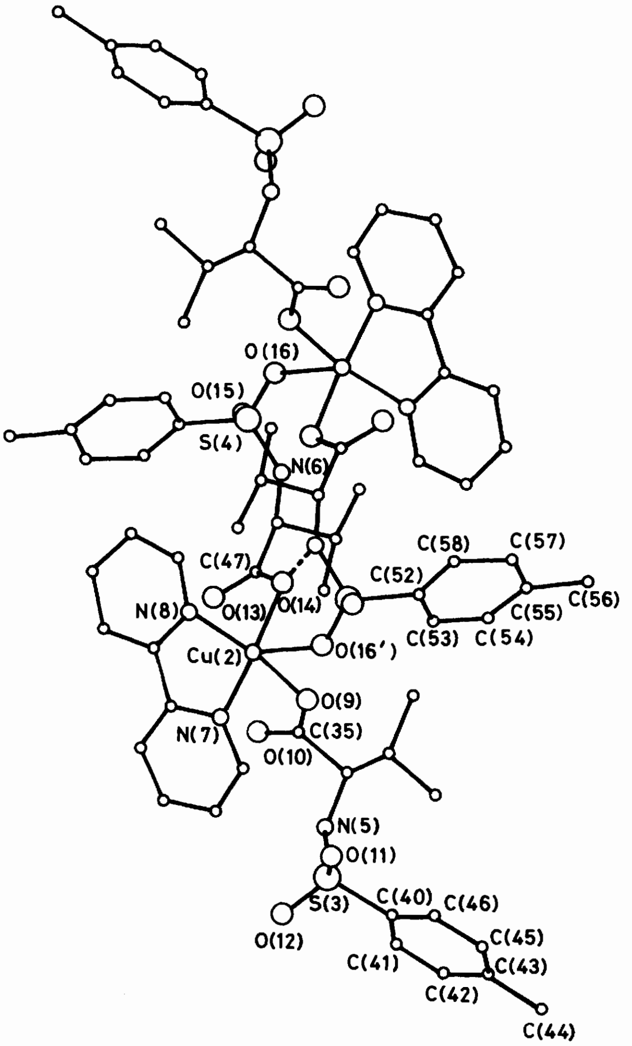

Figure 3. Clinographic projection of $[\{Cu(tsvalO)_2(bipy)\}_2]$, dimer (II)

Acknowledgements

The authors are grateful to the Centro di Calcolo Elettronico dell'Università di Modena and Parma for computing support and to the Centro Strumenti dell'Univeristà di Modena for recording e.s.r. spectra.

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Received 13*th May* 1986; *Paper* 6/910