Solid State and Ethanolic Solution Behaviour of *N*-Tosylglycinate–Copper(II) Complexes. Crystal and Molecular Structure † of a Strongly Coupled Polymeric *N*-Tosylglycinatocopper(II) Complex

Luciano Antolini, Ledi Menabue, and Gian Carlo Pellacani *
Istituto di Chimica Generale e Inorganica, University of Modena, Via Campi 183, 41100 Modena, Italy
Giovanna Battistuzzi Gavioli and Guilia Grandi
Istituto di Chimica Fisica, University of Modena, Via Campi 183, 41100 Modena, Italy
Luigi Pietro Battaglia and Anna Bonamartini Corradi
Istituto di Chimica Generale, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., University of Parma, Via D'azeglio 85, 43100 Parma, Italy
Giuseppe Marcotrigiano
Istituto di Chimica, Facoltà di Medicina-Veterinaria, University of Bari, Via Gentile 182, 70126 Bari, Italy

---

The interaction between *N*-tosylglycine and the copper(II) ion in ethanolic solution has been examined. Two compounds of formula $[\{Cu(tsglyO)_2\}_n]$ (green) and $Na_2[Cu(tsglyNO)_2]$ (blue) (tsglyO and tsglyNO = *N*-tosylglycinate monoanion and dianion, respectively) were isolated. Crystals of $[\{Cu(tsglyO)_2\}_n]$ are monoclinic, space group $P2_1/n$, with $Z = 4$ in a unit cell of dimensions $a = 24.655(3)$, $b = 7.697(2)$, $c = 12.378(3)$ Å, and $\beta = 87.34(8)°$. Full-matrix least-squares refinement, using 1 677 independent reflections, reached $R = 0.052$. The structure is built up of one-dimensional polymeric chains of binuclear units, showing the copper(II) acetate structure, linked *via* Cu–O(sulphonic) bonds. Its magnetic and spectroscopic properties are interpreted on the basis of the crystal structure. In particular it shows an exchange integral $(-2J)$ of 353 ± 4 and a zero-field splitting, *D*, of 0.35 cm^{-1}. The i.r. spectrum shows multiple sulphonamide absorption bands because only half of the SO_2 groups are co-ordinated. By polarographic measurements in ethanol, the number and type of complex species, the equilibria in which they are involved, and their stability constants have been determined. For $c_{NaOH}/c_{complex}$ ratios between 1 and 3 the species $[Cu(tsglyO)_2]$ is the only one present; for ratios >4, $[Cu(tsglyNO)_2]^{2-}$ prevails.

In this paper we report an investigation of the copper(II)–*N*-tosylglycinate system in ethanolic solution. The aim of this work is to determine polarographically the type, number, and stability constants of the complexes present in solution, and to characterize by means of structural, magnetic, and spectroscopic measurements those separated in the solid state and to compare them. The results can also be compared with those found for *N*-tosylglycine in aqueous solution [1] and with those found for the other *N*-protected (*N*-acetyl or *N*-benzoyl) amino acids, previously investigated in the same media.[2–5]

Experimental

Preparation of Polymeric N-*Tosylglycinatocopper*(II), $[\{Cu(tsglyO)_2\}_n]$.—By recrystallizing at room temperature bis(*N*-tosylglycinato)copper(II) tetrahydrate (prepared as reported in ref. 1*a*) from ethanol, green crystals precipitated (Found: C, 41.5; H, 3.90; N, 5.35; S, 12.3. Calc. for $C_{18}H_{20}CuN_2O_8S_2$: C, 41.55; H, 3.90; N, 5.40; S, 12.35%).

Physical Measurements.—Physical measurements were made on the solid complexes as described in ref. 1*a*. The polarographic measurements were performed with an AMEL Multipolarograph model 471; a saturated Ag/AgCl-KCl-C_2H_5OH electrode was used as reference electrode. All half-wave potentials were referred to a saturated calomel electrode (s.c.e.). All measurements were performed at constant temperature (25 ± 0.1 °C) and drop times were 2, 3, 4, or 6 s. The solutions ($[Cu^{2+}] = 1 \times 10^{-4}$ to 5×10^{-4} mol dm^{-3}) were prepared in anhydrous ethanol (C. Erba). $NaClO_4$, recrystallized from this solvent, was used as base electrolyte (0.1 mol dm^{-3}), and the ionic strength of the solution was kept constant ($I = 0.1$ mol dm^{-3}). The solution of Na(tsglyO) was prepared by dissolving in anhydrous ethanol an equimolar amount of *N*-tosylglycine and sodium hydroxide. The literature value of $E^{\circ}_{Cu^{2+}/Cu(Hg)} = 0.12$ V *vs.* s.c.e. was used to calculate the values of the stability constants.

As the polarographic reduction processes of the complexes are irreversible and diffusion controlled, their stability constants were determined using two different methods, which only give qualitative values. The first, (A), applied in the presence of ligand excess, uses equation (1) derived from a general expression for the current–voltage characteristic, valid for all degrees of reversibility and ligand concentrations:[6] β = overall stability constant of the complexes ($M^{n+} + nL^- \rightleftharpoons ML_n$); c_L = total ligand concentration; $c_L(0,t_1)$ = ligand concentration at the electrode surface and at time t_1; q = the greatest number of ligand molecules; p = number of co-ordinated ligand molecules of the complex reduced at the electrode.

The second method (B) replaces the concentrations in the expression of the stability constant with the current values of the species in equilibrium in solution, since, being diffusive, the currents are proportional to their concentrations. In this method the diffusion coefficients of all the species are considered equal, their activity coefficients equal to unity, and the current values are approximate to within *ca.* 10%.

---

† *Supplementary data available* (No. SUP 23944, 19 pp.): H-atom co-ordinates, thermal parameters, bond distances and angles in the tosyl groups, least-squares planes, structure factors, electrochemical parameters. See Notices for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Non-S.I. units employed: G = 10^{-4}T, $\chi_{c.g.s.u.} = \chi_{S.I.} \times (10^6/4\pi)$.

$$\log\beta + q\log c_L = \log\left\{\frac{i_d - i}{i} - \left[\frac{c_L(0,t_1)}{c_L}\right]^{q-p} . \exp\frac{\alpha nF}{RT}\left[E - (E_{\frac{1}{2}})_{irr}\right]\right\} - \frac{nF}{2.3RT}(E - E^{\ominus}{}_{Cu}) = f(c_L) \qquad (1)$$

The dissociation constants of *N*-tosylglycine were determined by pH-metric titrations with a Praizious pH-Meter Knick, using an Ingold glass electrode as indicator electrode, and an aqueous s.c.e. as external reference electrode; a saturated aqueous NH_4NO_3 solution was used as a salt bridge. The glass electrode was calibrated with two buffer ethanolic solutions, of pH 5.08 and 8.31.[7]

E.s.r. measurements were performed on the same or more concentrated solutions than those used for the polarographic analyses ($[Cu^{2+}] \leqslant 5 \times 10^{-3}$ mol dm^{-3}).

X-Ray Data Collection.—Lauè symmetry, systematic extinctions, compatible only with space group $P2_1/n$, and approximate lattice constants were obtained from rotation and Weissenberg photographs (Cu-K_α radiation). The unit-cell dimensions were then refined by least-squares methods using 2θ values of 15 high-angle reflections accurately measured on an on-line single-crystal automated Siemens AED diffractometer. Three-dimensional intensity data were collected at room temperature with the selected crystal mounted with the *b* axis along the φ axis of the diffractometer. Details specific to the *X*-ray data collection and processing are reported in Table 1.

All data were corrected for Lorentz and polarization effects, but not for absorption in view of the small crystal size and absorption coefficient. Only the 1 677 observed reflections, placed on an (approximately) absolute scale by means of a Wilson plot, were used in the structure determination and refinement.

Solution and Refinement of the Structure.—Neutral-atom scattering factors were used,[8a] with anomalous dispersion corrections applied to all non-hydrogen atoms.[8b] Refinement was by full-matrix least squares with $\Sigma w(|F_o|-|F_c|)^2$ being minimized; discrepancy indices used below are $R = (\Sigma||F_o|-|F_c||)/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, where *w* is the weighting factor. Major calculations were performed on a CDC Cyber 7600 computer by using the SHELX76 system of programs[9] for Fourier and least-squares calculations, and the ORTEP plotting program for drawing.[10]

Table 1. Summary of crystal data collection

Diffractometer	Siemens AED
Radiation	Ni-filtered Cu-K_α (λ = 1.541 78 Å)
Temp. (θ_c/°C)	20 ± 2
Crystal system	monoclinic
Space group	$P2_1/n$ (C_{2h}^5, no. 14)
a/Å	24.655(3)
b/Å	7.697(2)
c/Å	12.378(3)
β/°	87.34(8)
U/Å^3	2 346.4
Molecular formula	$C_{18}H_{20}CuN_2O_8S_2$
M	519.85
Z	4
F(000)	1 060
D_c/g cm^{-3}	1.47
D_m/g cm^{-3}	1.48 (by flotation in $CHCl_3$)
Reflections measured	$\pm h, +k, +l$
Scan type	ω—2θ
θ range (°)	3—60
Lowest speed (° min^{-1})	2.5
Max. scan width (°)	1.10
Standards	1 every 50 reflections (no changes)
Collected reflections	3 644
Observed reflections	1 677 with $I > 2\sigma(I)$ *
Crystal size (mm)	~0.23 × 0.13 × 0.04
Absorption coefficient (cm^{-1})	31.9
Absorption correction	not applied

* $\sigma^2(I)$ = (total counts) + (0.01 × intensity)^2.

The non-hydrogen atoms were located by Patterson and Fourier techniques, and least-squares refinement of their positional and isotropic thermal parameters led to convergence at *R* = 0.097 and *R'* = 0.125. At this stage the hydrogen atoms, treated as fixed contributors, were added to the model at locations obtained from difference maps (13 atoms), or at their calculated positions (seven atoms). Further refinement, on which the Cu, S, O, and two C atoms were allowed to vibrate anisotropically improved the *R* and *R'* factors to 0.052 and 0.063, respectively. For the final cycle, the shifts in all the 190 varied parameters were < 0.05σ. A final difference density map was featureless, with no peaks higher than 0.8 e Å^{-3}. Unit weights were used at all stages; no trend of $\Sigma w(|F_o|-|F_c|)^2$ *vs.* $|F_o|$, sinθ, or Miller indices was observed. During the refinement, zero weight was assigned to ten strong low-order reflections, which may be affected by secondary extinction, or, more likely, by counting errors.

Final atomic co-ordinates are given in Table 2.

Results and Discussion

From an ethanolic solution of *N*-tosylglycine and copper(II) ion two compounds, one green of formula $[\{Cu(tsglyO)_2\}_n]$ (tsglyO = *N*-tosylglycinate anion) and one blue of formula $Na_2[Cu(tsglyNO)_2]$ (tsglyNO = *N*-tosylglycinate dianion: also deprotonated on the NH group), were separated. The latter complex, which precipitated in the presence of sodium hydroxide, shows spectroscopic properties identical to those of the analogous blue complex $K_2[Cu(tsglyNO)_2]$, isolated from aqueous solution.[1a] For this reason in this paper we treat only the physical properties of the solid green $[\{Cu(tsglyO)_2\}_n]$ complex.

Solid State Behaviour.—Description of the structure. Tables 3 and 4 contain selected bond lengths and angles, with atoms numbered as in Figure 1. A detailed view of the copper atom environment is shown in Figure 2.

The structure is composed of one-dimensional polymeric chains, extended along the *b* axis, of binuclear centrosymmetric $Cu_2(tsglyO)_4$ units. The co-ordination polyhedron shows the dimeric copper(II) acetate structure,[11-13] with four bidentate carboxylate groups forming *syn–syn* bridges between the copper atoms; the axial co-ordination site is occupied by a sulphonic O atom from a neighbouring $tsglyO^-$ ion, which links the dimeric units into linear chains. The same polymeric structure occurs in copper(II) 2-acetoxybenzoate,[14] where the oxygen atoms of the acetyl residue act as terminal ligands. The structural features of the co-ordination polyhedron compare well with those reported for many binuclear copper(II) carboxylate complexes.[2a,15-19] The Cu–O(carboxylic) bond distances, equal within one standard deviation, average 1.955(7) Å, and the unique Cu–O(sulphonic) bond length of 2.168(7) Å is consistent with previously reported Cu–O-(water) apical bond distances [2.161(2) Å in $[Cu(O_2CMe)_2(H_2O)]$,[13] 2.17(2) Å in $[\{Cu(o\text{-}BrC_6H_4CO_2)_2(H_2O)\}_2]$,[18] and 2.156(4) Å in $[\{Cu[O_2CCH_2CH_2NHC(O)Me]_2(H_2O)\}_2]\cdot 2H_2O$ (green form)[2a]]. The bridge lengths (the sum of Cu–O–C–O–Cu distances) of 6.41 and 6.42 Å, respectively, are within

Table 2. Atomic co-ordinates with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu	−0.037 9(1)	0.893 7(2)	0.531 6(1)	O(21)	0.017 7(2)	0.781 9(9)	0.614 8(6)
O(11)	−0.014 6(3)	0.740 1(9)	0.412 2(6)	O(22)	0.082 9(3)	0.972 3(9)	0.564 3(6)
O(12)	0.048 6(3)	0.931 7(9)	0.354 7(6)	C(21)	0.065 1(4)	0.838 5(14)	0.613 6(9)
C(11)	0.024 1(4)	0.790 4(15)	0.350 8(9)	C(22)	0.107 2(4)	0.742 4(14)	0.675 5(9)
C(12)	0.042 1(4)	0.668 8(14)	0.260 0(9)	N(2)	0.088 2(3)	0.564 7(11)	0.701 0(7)
N(1)	0.051 1(3)	0.490 7(10)	0.294 4(7)	S(2)	0.128 3(1)	0.448 3(4)	0.771 5(3)
S(1)	0.105 1(1)	0.450 0(3)	0.358 4(2)	O(23)	0.104 1(3)	0.279 9(10)	0.779 2(8)
O(13)	0.115 5(3)	0.581 2(10)	0.435 2(5)	O(24)	0.138 2(3)	0.540 9(12)	0.866 7(7)
O(14)	0.100 2(3)	0.274 3(9)	0.396 4(6)	C(23)	0.189 8(4)	0.430 4(15)	0.695 7(9)
C(13)	0.157 7(4)	0.450 4(14)	0.257 2(8)	C(24)	0.235 9(5)	0.520 1(17)	0.726 1(10)
C(14)	0.207 2(5)	0.516 7(15)	0.284 0(9)	C(25)	0.283 2(5)	0.508 6(18)	0.661 6(11)
C(15)	0.251 3(5)	0.497 6(17)	0.204 9(10)	C(26)	0.285 7(5)	0.416 9(18)	0.567 8(11)
C(16)	0.244 7(5)	0.425 8(17)	0.111 7(10)	C(27)	0.238 7(5)	0.329 7(17)	0.536 5(11)
C(17)	0.194 5(5)	0.363 8(18)	0.085 7(10)	C(28)	0.191 1(5)	0.335 4(15)	0.601 2(9)
C(18)	0.149 9(5)	0.377 7(16)	0.159 3(10)	C(29)	0.336 7(6)	0.403 8(22)	0.495 7(15)
C(19)	0.292 2(6)	0.404 3(21)	0.028 3(13)				

Table 3. Selected bond distances (Å) with estimated standard deviations in parentheses *

Cu–O(11)	1.957(7)	Cu–O(21)	1.951(7)	C(12)–N(1)	1.46(1)	C(22)–N(2)	1.48(1)
Cu–O(12′)	1.955(7)	Cu–O(22′)	1.958(7)	N(1)–S(1)	1.611(8)	N(2)–S(2)	1.620(9)
Cu–O(14″)	2.168(7)	Cu · · · Cu′	2.577(3)	S(1)–O(13)	1.419(7)	S(2)–O(23)	1.428(8)
O(11)–C(11)	1.25(1)	O(21)–C(21)	1.25(1)	S(1)–O(14)	1.435(7)	S(2)–O(24)	1.409(9)
O(12)–C(11)	1.25(1)	O(22)–C(21)	1.26(1)	S(1)–C(13)	1.76(1)	S(2)–C(23)	1.75(1)
C(11)–C(12)	1.51(1)	C(21)–C(22)	1.51(1)				

* Primed atoms: symmetry transformation $-x, 2-y, 1-z$. Doubly primed atoms: symmetry transformation $-x, 1-y, 1-z$.

Table 4. Selected bond angles (°) with estimated standard deviations in parentheses *

O(11)–Cu–O(12′)	169.6(4)	O(21)–Cu–O(14″)	91.2(3)	O(12′)–Cu–O(21)	89.9(3)	Cu–O(12′)–C(11′)	125.3(7)
O(11)–Cu–O(21)	86.8(3)	O(22′)–Cu–O(14″)	98.8(4)	O(12′)–Cu–O(22′)	90.7(3)	Cu–O(21)–C(21)	121.4(7)
O(11)–Cu–O(22′)	90.9(3)	O(14″)–Cu · · · Cu′	173.3(2)	O(12′)–Cu–O(14″)	92.6(3)	Cu–O(22′)–C(21′)	121.9(7)
O(11)–Cu–O(14″)	97.3(4)	Cu–O(11)–C(11)	117.3(7)	O(21)–Cu–O(22′)	169.9(4)	Cu–O(14″)–S(1″)	138.1(3)
O(11)–C(11)–O(12)	127(1)	O(21)–C(21)–O(22)	126(1)	N(1)–S(1)–C(13)	104.4(5)	N(2)–S(2)–C(23)	106.9(5)
O(11)–C(11)–C(12)	117(1)	O(21)–C(21)–C(22)	119(1)	O(13)–S(1)–O(14)	117.8(5)	O(23)–S(2)–O(24)	119.4(6)
O(12)–C(11)–C(12)	116(1)	O(22)–C(21)–C(22)	114(1)	O(13)–S(1)–C(13)	109.0(5)	O(23)–S(2)–C(23)	108.2(6)
C(11)–C(12)–N(1)	114(1)	C(21)–C(22)–N(2)	110(1)	O(14)–S(1)–C(13)	106.4(5)	O(24)–S(2)–C(23)	108.0(5)
C(12)–N(1)–S(1)	117.9(7)	C(22)–N(2)–S(2)	115.6(7)	S(1)–C(13)–C(14)	117.4(8)	S(2)–C(23)–C(24)	120.8(9)
N(1)–S(1)–O(13)	111.8(4)	N(2)–S(2)–O(23)	105.9(5)	S(1)–C(13)–C(18)	120.2(8)	S(2)–C(23)–C(28)	118.9(9)
N(1)–S(1)–O(14)	106.6(4)	N(2)–S(2)–O(24)	107.8(5)				

* See footnote of Table 3.

the range (6.40—6.46 Å) reported for most dimeric copper(II) carboxylate complexes.[15,16] A relevant feature appears to be the very short Cu · · · Cu′ separation [2.577(3) Å], only slightly longer than that (2.565 Å) in copper(II) propionate,[19] as a confirmation of the shortening of the copper–copper distances in the dimeric units of polymeric structures with respect to the discrete dimers.[16]

The copper atom is displaced from the least-squares plane of the four oxygen atoms (deviations ±0.001 Å from this plane) 0.171 Å towards the apical O atom, the shortest deviation yet discovered for a dimeric copper(II) carboxylate.[15]

The corresponding bond distances and bond angles within the two crystallographically independent tsglyO⁻ ligands are not significantly different, and compare well with those observed in other tosyl or sulphonic derivatives.[1a,20–25] As in copper(II) 2-acetoxybenzoate,[14] both the ligands are co-ordinated to two metal ions in the same binuclear unit, but, in addition, one is also bonded to the copper atom from an adjacent dimeric unit. Nevertheless, their mode of bonding appears rather surprising. There are no previous examples of bond interactions between sulphonamidic O atoms and metal ions. In square-pyramidal $[Cu(tsglyNO)(H_2O)_3]$ [1a] and in the distorted square-planar $K_2[Cu(tsglyNO)_2]$ complex [1a] the ligand acts as bidentate toward a single metal atom through the deprotonated amide nitrogen and one carboxylate oxygen atom, with only a weak Cu · · · O(sulphonic) axial interaction [2.717(3) Å] in the latter compound. Furthermore, dimeric copper(II) acetate structures of *N*-substituted amino acid complexes have previously been reported only for aquabis(*N*-acetylglycinato)copper(II),[2b] and for $[\{Cu[O_2CCH_2CH_2NHC(O)Me]_2(H_2O)\}_2]\cdot 2H_2O$ (green form).[2a]

The packing is determined by normal van der Waals distances, with only one intra-chain hydrogen-bond interaction, N(1)–H(1) · · · O(21) $(-x, 1-y, 1-z) = 2.89$ Å (N–H · · · O 135°).

Magnetic and spectroscopic measurements. The room-temperature e.s.r. spectrum (Table 5) of our compound, typical of dimeric or polymeric copper(II) carboxylates,[4] shows a zero-field splitting *D* parameter of 0.35 cm⁻¹. At 123 K the absorption of the lowest magnetic field shows the seven-line hyperfine splitting from the two equivalent copper nuclei ($A_{\parallel} = 77 \times 10^{-4}$ cm^{-1}).

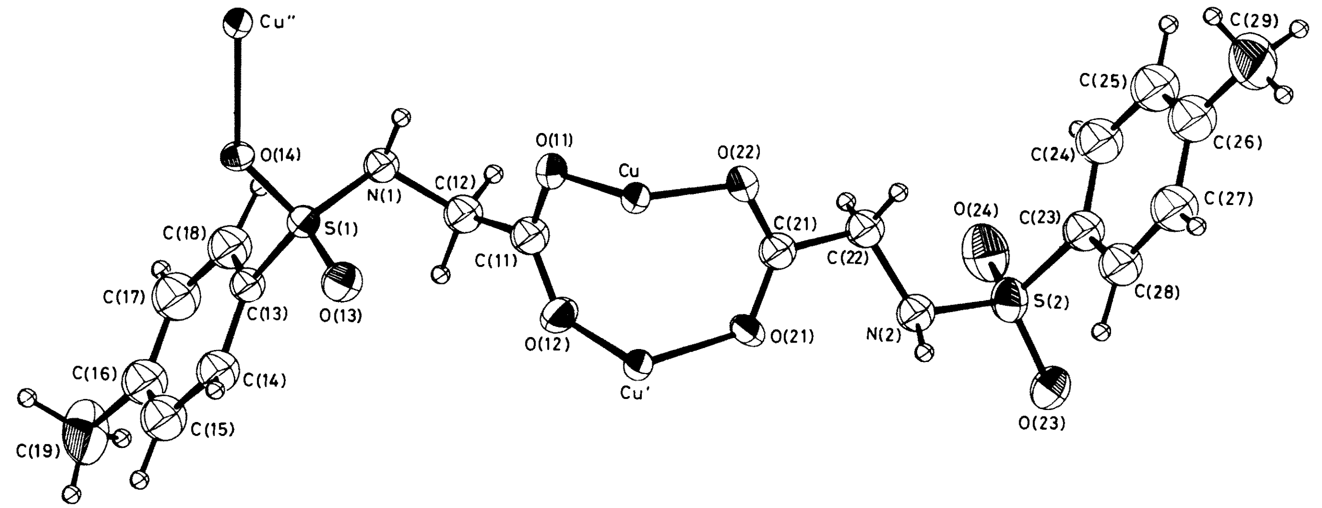

Figure 1. ORTEP drawing of [{Cu(tsglyO)$_2$}$_n$] showing the atom numbering and thermal ellipsoids (40%) for non-hydrogen atoms. The spheres of the hydrogen atoms are of arbitrary radius

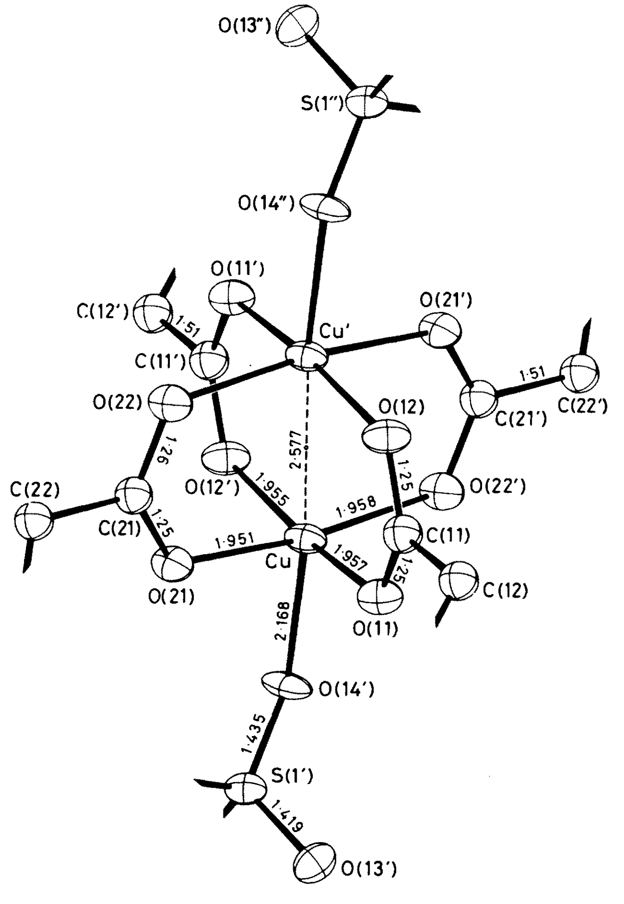

Figure 2. A portion of the linear-chain structure of [{Cu(tsglyO)$_2$}$_n$] with interatomic distances (Å)

Its magnetic susceptibility data, obtained on powdered samples over the temperature range 110—310 K, are indicative of binuclear species with strong antiferromagnetic exchange. The experimental data (Figure 3) were closely fitted by the Bleaney–Bowers equation for magnetically coupled pairs of copper(II) ions.[26] This equation was used unmodified, because very little amount of mononuclear impurities of spin $S = \frac{1}{2}$ were present, as observed in the region around 3 000 G of the e.s.r. spectra. By using for the Landè splitting factor $\bar{g} = [(g_{\parallel}^2 + 2g_{\perp}^2)/3]^{\frac{1}{2}}$ (ref. 27) the value of 2.180, determined by e.s.r., and for the Van Vleck temperature-independent constant $N\alpha = 60 \times 10^{-6}$ e.m.u. mol^{-1}, a $|2J|$ value of 353 ± 4 cm^{-1} is calculated, in agreement with those found for similar dimeric copper(II) *N*-protected amino acid and carboxylate complexes.[4]

Table 5. Room-temperature magnetic and spectroscopic results for the solid [{Cu(tsglyO)$_2$}$_n$] complex [a]

$g_{\parallel}$	2.363	D/cm^{-1}	0.35
$g_{\perp}$	2.083	$\lvert 2J\rvert$/cm^{-1}	353 ± 4
$\bar{g}$	2.180	$A_{\parallel}$/cm^{-1}	77 × 10^{-4}
$\mu_{eff.}$/B.M.	1.33		
Band I (ν/cm^{-1})	15 150		
Band II (ν/cm^{-1})	26 340		
ν(NH)/cm^{-1}	3 285s, 3 210s [b]		
ν(OCO)$_{asym}$/cm^{-1}	1 648vs		
ν(OCO)$_{sym}$/cm^{-1}	1 428vs		
ν(SO$_2$)$_{asym}$/cm^{-1}	1 340ms, 1 325s, 1 290s br [b]		
ν(SO$_2$)$_{sym}$/cm^{-1}	1 170s, 1 145s [b]		
ν(SN)/cm^{-1}	892m [b], 865m		

[a] The e.s.r. data are reported for the dimer. [b] Band associated with the co-ordinated SO$_2$ group.

The e.s.r. spectra show resolved copper hyperfine structure. Therefore, magnetic exchange between dimers through axially co-ordinated SO$_2$ groups is weaker than the hyperfine coupling.

The electronic spectrum of the complex (Table 5) is also characteristic of dimeric carboxylate-bridged structures.[16]

Its i.r. spectrum is assigned by comparison with those of other previously examined *N*-tosylglycinatocopper(II) complexes, in which the ligand is co-ordinated only through the carboxylate group.[1a] However, in agreement with the structural features of the present complex, in which 50% of the SO$_2$ groups are bonded to a copper atom, all the bands assignable to the sulphonamide group (NH, SO$_2$, SN) appear to split, as reported in Table 5.

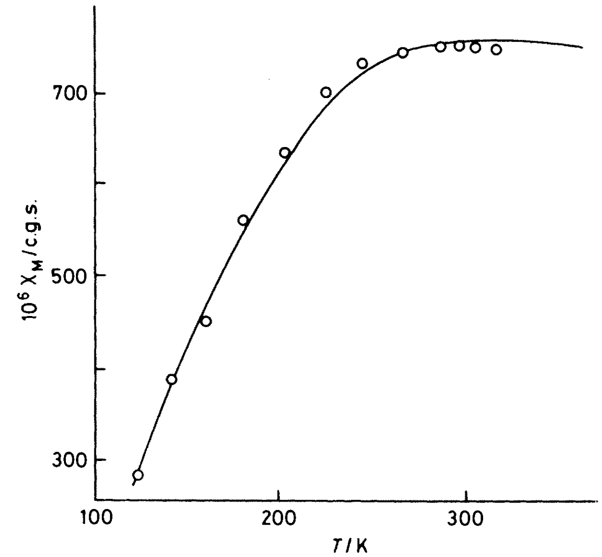

Figure 3. Corrected molar susceptibilities (○) and best-fit curve for the complex [{Cu(tsglyO)$_2$}$_n$]

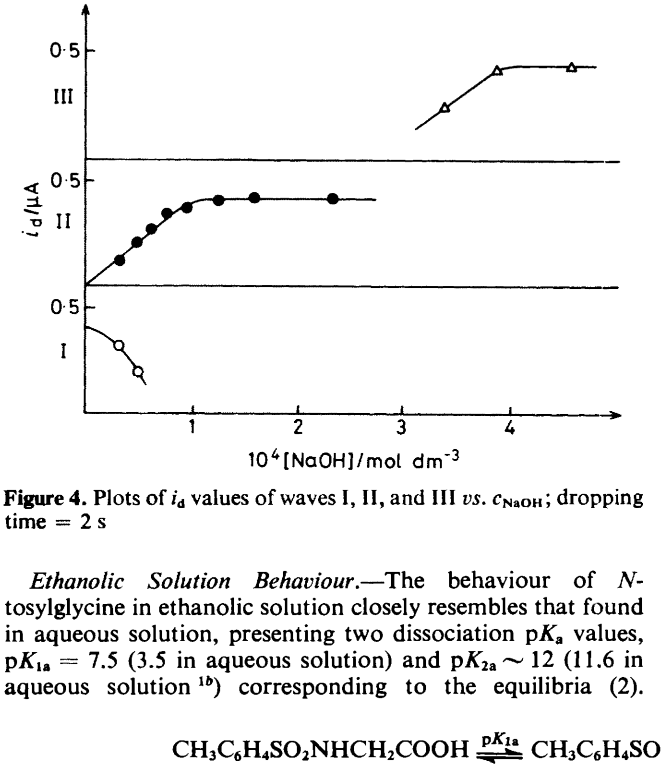

Figure 4. Plots of i_d values of waves I, II, and III *vs.* c_{NaOH}; dropping time = 2 s

Ethanolic Solution Behaviour.—The behaviour of *N*-tosylglycine in ethanolic solution closely resembles that found in aqueous solution, presenting two dissociation pK_a values, pK_{1a} = 7.5 (3.5 in aqueous solution) and pK_{2a} ~ 12 (11.6 in aqueous solution [1b]) corresponding to the equilibria (2).

$$\underset{\text{(tsgly)}}{CH_3C_6H_4SO_2NHCH_2COOH} \xrightleftharpoons{pK_{1a}} \underset{\text{(tsglyO}^-\text{)}}{CH_3C_6H_4SO_2NHCH_2COO^-} \xrightleftharpoons{pK_{2a}} \underset{\text{(tsglyNO}^{2-}\text{)}}{CH_3C_6H_4SO_2\overset{-}{N}CH_2COO^-} \quad (2)$$

Therefore for this amino acid any type of zwitterionic character may be excluded in ethanol also.

The polarographic curve of the [{Cu(tsglyO)$_2$}$_n$] or [Cu(tsglyO)$_2$]·4H$_2$O complexes in ethanol presents a well defined, quasi-reversible reduction wave (wave I) very similar to that found for the free copper(II) ion reduction [$E_{\frac{1}{2}}$ = +0.26 V *vs.* s.c.e.; αn = 0.89 (α = charge-transfer coefficient; n = number of electrons)], suggesting that the complexes are completely dissociated. By adding to these solutions of the complexes increasing amounts of an ethanolic NaOH solution (0.1 mol dm^{-3}), a new wave (wave II) appears, which has a more negative $E_{\frac{1}{2}}$ value and shows an increase of the limiting current value with increasing amounts of base, while wave I decreases until it disappears.

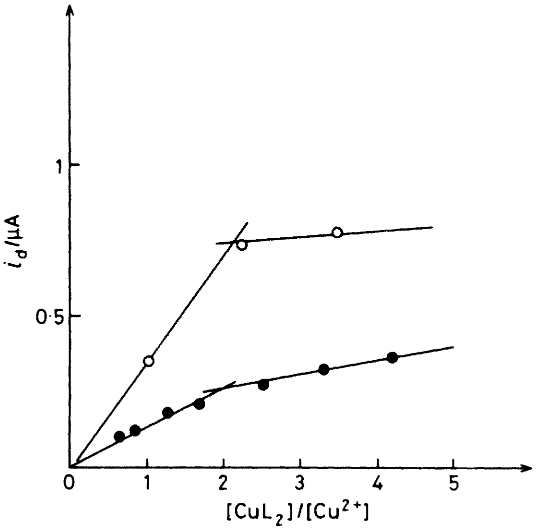

Figure 5. Plots of i_d(II) values *vs.* the molar ratio of the complex (L = tsglyO$^-$) to Cu^{2+} ion concentration at two different initial concentrations: (●) $c_{Cu^{2+}}$ = 10^{-4} mol dm^{-3}; (○) $c_{Cu^{2+}}$ = 2.5 × 10^{-4} mol dm^{-3}

The $E_{\frac{1}{2}}$ and i_d values of wave II are constant for $c_{NaOH}/c_{complex}$ ratios between 1 and 3 ($E_{\frac{1}{2}}$ = 0.070 V; Figure 4); for ratios > 3, a third wave (wave III) appears at more negative potential values, whose $E_{\frac{1}{2}}$ value remains constant ($E_{\frac{1}{2}}$ = −0.275 V) and limiting current values increase for increasing base concentration. The sum of the limiting current values of waves I and II and of waves II and III, respectively, remains nearly constant (Figure 4). For $c_{NaOH}/c_{complex}$ ratios > 4 a blue complex of formula Na$_2$[Cu(tsglyNO)$_2$] precipitated.

To determine the physicochemical characteristics of the species present in ethanolic solution, the Na(tsglyO)–Cu^{2+} system was investigated at varying tsglyO$^-$ concentrations. For a deficiency of ligand two waves (I and II) appear, corresponding to the reduction of Cu^{2+} ion and of [Cu(tsglyO)$_2$] complex, respectively; at increasing ligand concentration only wave II is present. The sharp break of Figure 5 [i_d(II) *vs.* ligand/metal ion molar ratios] corresponding to a molar ratio of 2, indicating the number of ligand molecules co-ordinated to the Cu^{2+} ion, is independent of the initial concentration of the metal ion.[28] Furthermore, the $E_{\frac{1}{2}}$ value of wave II does not vary even in the presence of a ligand excess. The reduction process then may be summarized by equation (3). This [Cu(tsglyO)$_2$] complex corresponds to that

$$[Cu(tsglyO)_2] + 2e^- \xrightarrow{\text{Hg electrode}} Cu(Hg) + 2\ tsglyO^-\ \text{(wave II)} \quad (3)$$

prevailing in aqueous solution in the pH range 5—7.5, for which the amino acid co-ordination through the carboxylate group has been suggested previously.[1b]

By adding small amounts of base to the solution of the [Cu(tsglyO)$_2$] complex, the third wave (wave III) appears, disappearing when the $c_{NaOH}/c_{Na(tsglyO)}$ ratio is greater than 2 for the precipitation of the $Na_2[Cu(tsglyNO)_2]$ compound, in which the ligand co-ordinates through the amidic and carboxylate groups, the hydrogen atom of the NH group being dissociated. {This complex shows physicochemical properties very similar to those of the blue complex $K_2[Cu(tsglyNO)_2]$, previously examined.[1a]} Therefore wave III corresponds to the reduction process of the $[Cu(tsglyNO)_2]^{2-}$ complex: equation (4).

$$[\mathrm{Cu(tsglyNO)_2}]^{2-} + 2\mathrm{e}^- \xrightarrow{\mathrm{Hg}} \mathrm{Cu(Hg)} + 2\,\mathrm{tsglyNO}^{2-} \qquad (4)$$

Analysis of waves II *and* III. The semi-logarithmic analysis of wave II shows that the reduction is irreversible and a diffusion-controlled process and the value of the overall stability constant (β_2) of $[Cu(tsglyO)_2]$ obtained is 10^8 (method A) and 1.5×10^8 (method B). In agreement with the acceptor–donor properties of the solvent [29] the $[Cu(tsglyO)_2]$ complex appears to be slightly more stable in ethanol than in water.[1b]

The semi-logarithmic analysis of wave III shows that the reduction of the $[Cu(tsglyNO)_2]^{2-}$ complex is also an irreversible, two-electron diffusion-controlled process; a value for β_3 of 3×10^{19} was calculated using method A.

The chemical equilibria and the overall electrochemical reduction process, as a function of NaOH concentration, may be summarized as shown below, where $\beta_2 = K_2$ and $\beta_3 = K_2K_3$. Therefore, the stability constant (K_3) of the $[Cu(tsglyNO)_2]^{2-}$ complex referred to the $[Cu(tsglyO)_2]$ complex being equal to 10^{10} (calculated using method B), a value of 1.5×10^{18} is obtained for β_3, in agreement with the value from method A.

$$\begin{tikzcd}
\mathrm{Cu^{2+}} + 2\mathrm{tsglyO^-} \arrow[r, "\text{wave I}", "\text{Hg, 2e}^-"'] \arrow[d, shift left, "K_2"] & \mathrm{Cu(Hg)}\ (E_{\frac{1}{2}} = 0.26\ \mathrm{V}) \\
\mathrm{[Cu(tsglyO)_2]} + 2\,\mathrm{OH^-} \arrow[u, shift left] \arrow[r, "\text{wave II}", "\text{Hg, 2e}^-"'] \arrow[d, shift left, "K_3"] & \mathrm{Cu(Hg)} + 2\,\mathrm{tsglyO^-}\ (E_{\frac{1}{2}} = 0.07\ \mathrm{V}) \\
\mathrm{[Cu(tsglyNO)_2]^{2-}} + 2\,\mathrm{H_2O} \arrow[u, shift left] \arrow[r, "\text{wave III}", "\text{Hg, 2e}^-"'] & \mathrm{Cu(Hg)} + 2\,\mathrm{tsglyNO^{2-}}\ (E_{\frac{1}{2}} = -0.27\ \mathrm{V})
\end{tikzcd}$$

Acknowledgements

We thank the Centro Strumenti of the University of Modena for the recording of the i.r. spectra, the Centro di Calcolo of the University of Modena for the computing facilities, and the Ministero della Pubblica Istruzione of Italy for financial support.

References

1 (*a*) L. Antolini, L. P. Battaglia, G. Battistuzzi Gavioli, A. Bonamartini Corradi, G. Grandi, G. Marcotrigiano, L. Menabue, and G. C. Pellacani, *J. Am. Chem. Soc.*, 1983, **105**, 4327; (*b*) 1983, **105**, 4333.

2 (*a*) L. P. Battaglia, A. Bonamartini Corradi, G. Marcotrigiano, L. Menabue, and G. C. Pellacani, *Inorg. Chem.*, 1981, **20**, 1075 and refs. therein; (*b*) M. R. Udupa and B. Krebs, *Inorg. Chim. Acta*, 1979, **37**, 1.

3 (*a*) G. Battistuzzi Gavioli, G. Grandi, G. Marcotrigiano, L. Menabue, G. C. Pellacani and M. Tonelli, Proceedings XI Congresso Nazionaledi Chimica Inorganica, Arcavacata di Rende (Cosenza), Italy, September 1978, p. 4e; (*b*) R. Andreoli, G. Battistuzzi Gavioli, L. Benedetti, G. Grandi, G. Marcotrigiano, L. Menabue, and G. C. Pellacani, *Inorg. Chim. Acta*, 1980, **46**, 215 and refs. therein.

4 L. Antolini, L. Menabue, P. Prampolini, and M. Saladini, *J. Chem. Soc., Dalton Trans.*, 1982, 2109 and refs. therein.

5 H. B. Gray, in 'Bioinorganic Chemistry,' Adv. Chem. Ser. No. 100, American Chemical Society, Washington D.C., 1971, pp. 365—389 and refs. therein.

6 N. G. Elenkova and T. K. Nedelcheva, *J. Electroanal. Chem.*, 1976, **69**, 385, 393.

7 D. D. Perrin and B. Dempsey, 'Buffers of pH and Metal Ion Control,' Chapman and Hall, London, 1979, p. 90.

8 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, (*a*) pp. 99—101; (*b*) pp. 149—150.

9 G. M. Sheldrick, SHELX76 program for crystal structure determination, University of Cambridge, 1976.

10 C. K. Johonson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.

11 J. N. Niekerk and F. R. L. Schoening, *Acta Crystallogr.*, 1953, **6**, 227.

12 P. de Meester, S. R. Fletcher, and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 1973, 2575.

13 G. M. Brown and R. Chidambaram, *Acta Crystallogr., Sect. B*, 1973, **29**, 2393.

14 L. Manojlovic-Muir, *Acta Crystallogr., Sect. B*, 1973, **29**, 2033.

15 R. J. Doedens, *Prog. Inorg. Chem.*, 1976, **21**, 209 and refs. therein.

16 J. Catterick and P. Thornton, *Adv. Inorg. Chem. Radiochem.*, 1977, **20**, 291 and refs. therein.

17 R. McCrindle, G. Ferguson, A. J. McAless, and P. J. Roberts, *J. Chem. Soc., Dalton Trans.*, 1981, 1406.

18 W. Harrison, S. Rettig, and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 1972, 1852.

19 M. J. Bird and T. R. Lomer, *Acta Crystallogr., Sect. B*, 1972, **28**, 242.

20 E. R. Hessling, J. G. H. De Jong, A. R. Overbeek, and H. Schenk, *Cryst. Struct. Commun.*, 1973, **2**, 247.

21 (*a*) M. Cesario and J. Guilhelm, *Cryst. Struct. Commun.*, 1977, **6**, 707; (*b*) F. G. K. Smit and C. H. Stam, *ibid.*, 1978, **7**, 499.

22 J. Kay, M. D. Glick, and M. Raban, *J. Am. Chem. Soc.*, 1971, **93**, 5224.

23 A. Knöchel, J. Kopf, J. Oelher, and G. Rudolph, *J. Chem. Soc., Chem. Commun.*, 1978, 595.

24 C. Couldwell, K. Prout, D. Robey, R. Taylor, and F. J. Rossotti, *Acta Crystallogr., Sect. B*, 1978, **34**, 1491.

25 T. Graafland, A. Wagenaar, A. J. Kirby, and J. B. F. N. Engberts, *J. Am. Chem. Soc.*, 1979, **101**, 6981.

26 B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, 1952, **214**, 451.

27 R. W. Jotham and S. F. Kettle, *J. Chem. Soc. A*, 1969, 2816.

28 K. Ogura, Y. Fukusima, and I. Aomizu, *J. Electroanal. Chem.*, 1980, **107**, 271.

29 V. Gutman and R. Schmid, *Coord. Chem. Rev.*, 1974, **12**, 263; V. Gutman, *ibid.*, 1976, **18**, 225.

Received 10*th October* 1983; *Paper* 3/1789