

The Role of the Tosyl Group on the Coordination Ability of N-Protected Amino Acids. 1. Solid-State Behavior of (N-Tosylglycinato)copper(II) Complexes: Crystal and Molecular Structures of (N-Tosylglycinato)triaquacopper(II) and Dipotassium Bis(N-tosylglycinato)copper(II) Complexes

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Abstract: The interaction between *N*-tosylglycine and the copper(II) ion in aqueous solution at different pH values gives rise to the formation of four compounds of formula $\text{Cu}(\text{TsglyH})_2 \cdot 4\text{H}_2\text{O}$, $[\text{Cu}(\text{Tsgly})(\text{H}_2\text{O})_3]$, and $\text{K}_2[\text{Cu}(\text{Tsgly})_2]$, which exists in two forms, one blue and one violet (TsglyH = *N*-tosylglycinate ion; Tsgly = *N*-tosylglycinate dianion). All the compounds were characterized by means of thermal, spectroscopic, magnetic, and structural measurements. For two compounds, the $[\text{Cu}(\text{Tsgly})(\text{H}_2\text{O})_3]$ and $\text{K}_2[\text{Cu}(\text{Tsgly})_2]$ (blue form), the crystal structures were also determined by three-dimensional X-ray diffraction. The $[\text{Cu}(\text{Tsgly})(\text{H}_2\text{O})_3]$ complex crystallizes in the monoclinic $P2_1/c$ space group with four molecules in the unit cell of dimensions $a = 13.690$ (1) Å, $b = 10.333$ (1) Å, $c = 10.556$ (1) Å, and $\beta = 109.03$ (1)°. Least-squares refinement of 232 variables led to a conventional *R* index of 0.043 for 1735 independent reflections. Coordination around the copper is tetragonal pyramidal with the nitrogen atom, one carboxylate oxygen and two water molecules at the basis and another water molecule in the apical position. The $\text{K}_2[\text{Cu}(\text{Tsgly})_2]$ complex crystallizes in the triclinic $P\bar{1}$ space group with two molecules in the unit cell of dimensions $a = 9.662$ (2) Å, $b = 10.200$ (1) Å, $c = 12.921$ (2) Å, $\alpha = 80.36$ (1)°, $\beta = 88.24$ (1)°, and $\gamma = 62.94$ (1)°. Least-squares refinement of 298 variables led to a conventional *R* index of 0.043 for 2189 independent reflections. The structure consists of $[\text{CuL}_2]^{2-}$ anions and potassium cations. Coordination around the copper is square planar, tetrahedrally distorted and involves two carboxylic oxygen and two nitrogen atoms. A long contact with a sulfonic oxygen atom completes the coordination to 4 + 1 terms. Spectroscopic and magnetic results in the light of known structures were used to recognize the active binding sites on the ligand and the stereochemistries of the structurally unknown complexes. The *N*-tosylglycine shows a double behavior: at pH < 5 it acts as a simple carboxylic acid (in the $\text{Cu}(\text{TsglyH})_2 \cdot 4\text{H}_2\text{O}$ complex), while at pH > 5 it acts as a polypeptidic ligand. In fact, the deprotonation of the NH group accompanied by the nitrogen atom coordination may take place at a pH lower than that expected by its pK_a values.

Copper(II) complexes of amino acids have been studied in considerable detail, and, if there are no complicating donor side chains, the acids coordinate solely through the amino and carboxylate groups, forming stable five-membered-chelate rings with the metal ions, as found for each of the 20 or so naturally occurring L- α -amino acids.²⁻⁴

The introduction of a substituent, such as an acetyl or a benzoyl group, diminishing the affinity of the amino group for the metal ions, reduces the ligand field of the in-plane donor. As a consequence, the acids invariably coordinate solely through the carboxylic group, which may act as monodentate or bidentate ligand, permitting the copper(II) ion to assume various geometries and to form easy ternary complexes with amines.^{5,6} In these

systems, as the peptidic group remains planar, it turns out to be involved in only hydrogen bonding with other peptidic groups and/or water molecules (if present) in the crystal packing.^{5a,b,d,6e,i,k} This agrees with previous results in which the O(peptide) atom was found to coordinate only when stabilized by the closure of a chelate ring with an adjacent terminal amino group and the N(peptide) atom was found to bind a metal only when the process is accompanied by the dissociation of the peptide proton.⁷

Our interest in the coordinative properties of N-protected amino acids⁶ is now extended to the study of the *N*-tosyl derivatives, since by utilizing a tosyl group (Figure 1) as a protecting group, in place

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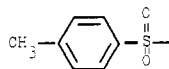


Figure 1. 4-Toluenesulfonyl (or tosyl) group.

of an acetyl or a benzoyl group, different chemical results may be expected.

In fact the tosyl group shows the "desirable" property that the substituted amino group can react further, as, the sulfonyl group having a strong inductive electrophilic effect, the anion of the sulfonamide group becomes an excellent nucleophile.⁸

In this paper we report an investigation on the solid-state behavior of the (*N*-tosylglycinato)copper(II) complexes separated from aqueous solution. The compounds were studied by means of thermogravimetric, spectroscopic, magnetic, and structural measurements. This article is indicated as part 1. In a second paper (indicated as part 2 (see the following article)) we examine the behavior of the same systems in aqueous solution. Although the two parts are obviously strictly correlated one with the other, the abundance of material has led us to publish them separately.

Experimental Section

Preparation of Bis(*N*-tosylglycinato)copper(II) Tetrahydrate Complex, $\text{Cu}(\text{TsglyH})_2 \cdot 4\text{H}_2\text{O}$. The compound was prepared by adding a boiling copper acetate monohydrate (1.25 mmol) aqueous solution to a cold aqueous solution of *N*-tosylglycine (2 mmol). With cooling at room temperature a blue crystalline compound (not useful for X-ray structural analysis) separated. The same compound separated after evaporation of a blue solution containing *N*-tosylglycine and copper(II) hydroxide (freshly prepared) in the molar ratio of 2:1. Anal. Calcd for $\text{C}_{18}\text{H}_{28}\text{CuN}_2\text{O}_{12}\text{S}_2$: C, 36.49; H, 4.76; N, 4.73; S, 10.83. Found: C, 36.48; H, 4.70; N, 4.65; S, 10.74.

Preparation of (*N*-Tosylglycinato)triaquacopper(II) Complex, $[\text{Cu}(\text{Tsgly})(\text{H}_2\text{O})_3]$. Blue crystals were obtained by recrystallizing the bis-(*N*-tosylglycinato)copper(II) tetrahydrate from aqueous solution at room temperature. Anal. Calcd for $\text{C}_9\text{H}_{15}\text{CuNO}_7\text{S}$: C, 31.33; H, 4.39; N, 4.06; S, 9.30. Found: C, 31.31; H, 4.48; N, 4.05; S, 9.23.

Preparation of Dipotassium Bis(*N*-tosylglycinato)copper(II) Complex, $\text{K}_2[\text{Cu}(\text{Tsgly})_2]$, One Form Violet and One Form Blue. Violet crystals separated by reaction of *N*-tosylglycine (2 mmol) and copper(II) acetate monohydrate (1 mmol) in water by addition of potassium hydroxide until a limpid deep blue solution was obtained and evaporation (40 °C) of the solution under vacuum. The violet crystals were washed with ethanol and diethyl ether and dried on P_2O_5 under vacuum. Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{CuN}_2\text{O}_8\text{S}_2\text{K}_2$: C, 36.24; H, 3.04; N, 4.70; S, 10.76. Found: C, 36.20; H, 3.05; N, 4.69; S, 10.66.

Light-blue crystals (blue form) were obtained by evaporation in air of the blue solution from which violet crystals were previously separated. The crystals were washed with ethanol and diethyl ether and dried on P_2O_5 under vacuum. Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{CuN}_2\text{O}_8\text{S}_2\text{K}_2$: C, 36.24; H, 3.04; N, 4.70; S, 10.76. Found: C, 36.18; H, 2.98; N, 4.65; S, 10.60.

Physical Measurements. Physical measurements were made as described in ref 6j) and 6k).

X-ray Data Collection and Structure Determination. The most relevant crystal data for both compounds are given in Table I. Cell dimensions were measured by diffractometry with an "on line" single-crystal automated Siemens AED diffractometer and refined by least-squares procedure with use of θ values of 15 high-angle reflections ($110 \leq 2\theta \leq 120^\circ$) accurately measured. One reflection was measured after every 50 reflections as a check on alignment and on the crystal and instrument stability. The individual reflection profiles were analyzed as described by Grant and Gabe.⁹ After the usual Lorentz and polarization corrections, the structure amplitudes were put on absolute scale by least squares. The correction for absorption was applied only to the data of complex II, its transmission factors ranging from 0.31 to 0.66. For complex I, no correction for absorption was applied, as the μ_r value was very low (0.32) and the absorption correction coefficients were practically unchanged in 2–60° θ range, assuming a cylindrical shape for the crystal. For both compounds, the structure was solved by conventional Patterson and Fourier methods and refined anisotropically by several full-matrix least-squares cycles. The hydrogen atoms were located from $F_o - F_c$ maps for both compounds and for I were refined isotropically to the *R* index of 0.043. In complex II, the hydrogen atoms were not refined but are included in the final structure factor calculation. The final *R* index was

Table I. Crystal Data for the Complexes

	$[\text{Cu}(\text{Tsgly})(\text{H}_2\text{O})_3]$ (I)	$\text{K}_2[\text{Cu}(\text{Tsgly})_2]$ (II)
molecular formula	$\text{C}_9\text{H}_{15}\text{CuNO}_7\text{S}$	$\text{C}_{18}\text{H}_{18}\text{CuK}_2\text{N}_2\text{O}_8\text{S}_2$
mol wt	344.83	596.21
<i>a</i> , Å	13.690 (1)	9.662 (2)
<i>b</i> , Å	10.333 (1)	10.200 (1)
<i>c</i> , Å	10.556 (1)	12.921 (2)
α , deg	90.0	80.36 (1)
β , deg	109.03 (1)	88.24 (2)
γ , deg	90.0	62.94 (1)
<i>V</i> , Å ³	1411.6 (2)	1116.5 (3)
<i>Z</i>	4	2
<i>d</i> _{calcd} , g·cm ⁻³	1.62	1.77
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
crystal dimens, mm	0.10 × 0.26 × 0.36	0.10 × 0.16 × 0.20
radiation (λ , Å)	Cu K α ($\lambda = 1.54178$) (Ni filtered)	Cu K α ($\lambda = 1.54178$) (Ni filtered)
2 θ limits, deg	4–120	4–140
scan technique	ω -2 θ	ω -2 θ
temp, °C	20	20
abs coeff, cm ⁻¹	37.82	69.45
<i>F</i> (000), electrons	708	606
unique data used	1735	2189
(<i>I</i> > 2 σ) ^a		
no. of variables	232	298
<i>R</i>	0.043	0.043
<i>R</i> _w ^b	0.046	0.042
<i>g</i>	7.7×10^{-3}	14.7×10^{-3}

^a $\sigma^2(I) = \text{total counts} + (0.001 \text{ intensity})^2$. ^b Weighting scheme $w^{-1} = [\sigma^2(F_o) + g(F_c)^2]$.

4.3%. The atomic scattering factors used, corrected for the anomalous dispersion, were taken from the International Tables.¹⁰ Five reflections (–111, 113, –202, 100, 202) were excluded from the final refinement of I, as they had been affected by extinction or counting errors. For both compounds, all the calculations were performed with the use of CYBER 76 of the Centro di Calcolo dell'Italia Nord-Orientale, Bologna, with the SHELX system of programs.¹¹ Final atomic coordinates are quoted in Tables II and III for $[\text{Cu}(\text{Tsgly})(\text{H}_2\text{O})_3]$ and $\text{K}_2[\text{Cu}(\text{Tsgly})_2]$, respectively.

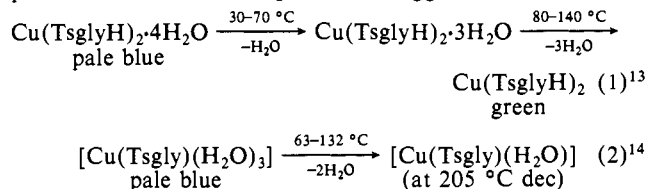
Analysis. Sulfur, nitrogen, carbon, and hydrogen were analyzed with a C. Erba Elemental Analyser Instrument Model 1106 by G. Pistoni.

Results and Discussion

The behavior of *N*-tosylglycine toward the copper(II) ion, in aqueous solution, is strictly dependent on the pH of the solution. In fact at pH ≈ 3.7 a compound of formula $\text{Cu}(\text{TsglyH})_2 \cdot 4\text{H}_2\text{O}$ ($\text{TsglyH} = N$ -tosylglycinate monoanion) was separated, while from the dissolution of this complex in water (pH 4–5) a compound of formula $[\text{Cu}(\text{Tsgly})(\text{H}_2\text{O})_3]$ ($\text{Tsgly} = N$ -tosylglycinate dianion (in which the NH group was also deprotonated)) precipitated. The presence of the sulfonyl group in tosylglycine permits the deprotonation of the N–H group, accompanied by the formation of a metal–N bond. This deprotonation at very low pH (~ 5) is favored by the presence of a copper(II) ion in the $\text{Cu}(\text{TsglyH})_2 \cdot 4\text{H}_2\text{O}$ complex. This was also observed in the deprotonation in some glycine peptide ligands.^{7,12}

At pH > 10 the *N*-tosylglycine also parallels the behavior of some glycine ligands,^{7,12} separating two compounds, one blue and one violet, of formula $\text{K}_2[\text{Cu}(\text{Tsgly})_2]$.

The thermogravimetric behavior of the two hydrated compounds, summarized in eq 1 and 2, suggests that in the first



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Table II. Fractional Atomic Coordinates ($\times 10^4$) for the $[\text{Cu}(\text{Tsgly})(\text{H}_2\text{O})_3]$ Complex

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Cu	554 (1)	-50 (1)	1953 (1)	C(8)	4404 (6)	-2046 (8)	4109 (9)
S	2237 (1)	-1116 (1)	650 (1)	C(9)	3491 (5)	-1963 (7)	3073 (7)
O(1)	680 (3)	1809 (4)	1906 (4)	H(1)	2661 (53)	1438 (65)	1607 (68)
O(2)	1379 (4)	3431 (3)	1134 (4)	H(2)	1847 (50)	1587 (65)	-72 (75)
O(3)	2489 (4)	-806 (4)	-554 (4)	H(3)	4268 (57)	-99 (61)	956 (89)
O(4)	1718 (3)	-2354 (3)	639 (4)	H(4)	5903 (53)	-413 (75)	2944 (68)
O(5)	-666 (3)	232 (4)	2571 (5)	H(5)	6936 (66)	-1255 (79)	5065 (82)
O(6)	192 (4)	-1858 (4)	1618 (5)	H(6)	6479 (58)	-2252 (75)	5801 (75)
O(7)	1484 (4)	-290 (4)	4142 (4)	H(7)	6303 (52)	-925 (77)	5843 (70)
N	1546 (4)	-13 (4)	965 (5)	H(8)	4425 (55)	-2509 (68)	4785 (85)
C(1)	1290 (4)	2268 (5)	1316 (5)	H(9)	2847 (55)	-2506 (61)	3186 (65)
C(2)	1935 (5)	1301 (5)	837 (6)	H(10)	-897 (59)	-466 (78)	3105 (79)
C(3)	3428 (5)	-1229 (5)	1948 (6)	H(11)	-1268 (54)	535 (71)	1958 (72)
C(4)	4303 (5)	-540 (8)	1923 (8)	H(12)	-117 (64)	-2271 (73)	1993 (88)
C(5)	5223 (6)	-659 (9)	2991 (9)	H(13)	819 (65)	-2213 (75)	1920 (78)
C(6)	5278 (6)	-1417 (7)	4100 (9)	H(14)	1541 (61)	-895 (83)	4633 (82)
C(7)	6217 (6)	-1512 (12)	5248 (14)	H(15)	1468 (57)	197 (81)	4696 (80)

Table III. Fractional Atomic Coordinates ($\times 10^4$) for the $\text{K}_2[\text{Cu}(\text{Tsgly})_2]$ Complex

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Cu	3722 (1)	3513 (1)	1114 (1)	C(12)	2408 (8)	1187 (8)	3270 (6)
K(1)	3422 (2)	1494 (2)	-749 (1)	C(13)	3227 (12)	1781 (13)	3694 (8)
K(2)	995 (2)	-1511 (2)	1194 (1)	C(14)	3334 (13)	1724 (15)	4765 (9)
S(1)	5513 (2)	5385 (2)	1664 (1)	C(15)	2634 (11)	1069 (11)	5441 (7)
S(2)	2310 (2)	1219 (2)	1890 (2)	C(16)	2774 (13)	933 (14)	6628 (8)
O(1)	5412 (5)	1654 (5)	805 (4)	C(17)	1789 (16)	505 (14)	5021 (9)
O(2)	7956 (5)	450 (5)	630 (4)	C(18)	1654 (14)	571 (13)	3936 (8)
O(3)	3970 (5)	6578 (5)	1742 (4)	H(1)	7391 (0)	3320 (0)	468 (0)
O(4)	6549 (5)	5817 (5)	1019 (4)	H(2)	7736 (0)	2474 (0)	1762 (0)
O(5)	1992 (5)	5420 (5)	1206 (4)	H(3)	7896 (0)	5867 (0)	2626 (0)
O(6)	-504 (5)	6623 (5)	1489 (5)	H(4)	8995 (0)	5104 (0)	4464 (0)
O(7)	3782 (5)	62 (5)	1649 (4)	H(5)	9191 (0)	3827 (0)	6366 (0)
O(8)	963 (6)	1000 (6)	1706 (4)	H(6)	7356 (0)	3980 (0)	6638 (0)
N(1)	5421 (6)	4018 (6)	1322 (5)	H(7)	8859 (0)	2292 (0)	6355 (0)
N(2)	2116 (6)	2777 (6)	1307 (5)	H(8)	6220 (0)	2877 (0)	5307 (0)
C(1)	6792 (7)	1545 (7)	827 (5)	H(9)	5173 (0)	3566 (0)	3494 (0)
C(2)	6953 (7)	2863 (7)	1106 (7)	H(10)	-251 (0)	4117 (0)	860 (0)
C(3)	6400 (7)	4780 (8)	2960 (6)	H(11)	156 (0)	3762 (0)	2216 (0)
C(4)	7516 (8)	5191 (10)	3234 (6)	H(12)	3824 (0)	2244 (0)	3187 (0)
C(5)	8141 (10)	4754 (12)	4245 (7)	H(13)	3967 (0)	2239 (0)	5069 (0)
C(6)	7696 (10)	3934 (12)	5011 (7)	H(14)	3476 (0)	1408 (0)	6997 (0)
C(7)	8334 (12)	3509 (14)	6127 (8)	H(15)	3324 (0)	-284 (0)	6997 (0)
C(8)	6587 (11)	3505 (12)	4724 (8)	H(16)	1575 (0)	1507 (0)	6928 (0)
C(9)	5984 (10)	3920 (11)	3709 (7)	H(17)	1208 (0)	-45 (0)	5547 (0)
C(10)	659 (7)	5463 (7)	1382 (6)	H(18)	939 (0)	109 (0)	3599 (0)
C(11)	545 (8)	4026 (8)	1443 (6)				

complex (eq 1) one water molecule is certainly not involved in strong hydrogen bonding in the crystal or is not coordinated with the copper(II) ion and that in the second complex (eq 2) only two coordinated (see structural results later) water molecules may be lost from the complex without its decomposing.

Description of the Structures. In the blue crystals of $[\text{Cu}(\text{Tsgly})(\text{H}_2\text{O})_3]$ the copper atom displays a 4 + 1 tetragonal pyramidal coordination, in which the deprotonated amide nitrogen, one carboxylate oxygen, and two water molecules characterize the basis of the pyramid and another water molecule the apex. The planarity analysis shows that the four equatorial atoms are coplanar, with the copper 0.220 (1) Å out of the plane toward the apex of the pyramid (O(7)), the angle between the Cu-O(7) vector with the normal to the equatorial plane being 10.2 (1)°. The chelation ring O(1)C(1)C(2)N(1)Cu forms a dihedral angle of 42.3 (1)° with the plane through the sulfonate group and of 81.3 (2)° with the benzene ring.

In Table IV bond distances and angles in the complex are quoted and Figure 2 reports the clinographic projection of the

Table IV. Bond Distances (Å) and Angles (deg) with esd's in Parentheses for the $[\text{Cu}(\text{Tsgly})(\text{H}_2\text{O})_3]$ Complex

(a) In the Coordination Polyhedron			
Cu-O(1)	1.931 (4)	Cu-O(6)	1.936 (4)
Cu-N	1.964 (6)	Cu-O(7)	2.259 (4)
Cu-O(5)	2.003 (5)	N-Cu-O(5)	164.7 (2)
O(6)-Cu-O(7)	96.1 (2)	O(1)-Cu-O(7)	96.3 (2)
O(5)-Cu-O(7)	86.2 (2)	O(1)-Cu-O(6)	167.2 (2)
O(5)-Cu-O(6)	90.5 (2)	O(1)-Cu-O(5)	87.4 (2)
N-Cu-O(7)	106.8 (2)	O(1)-Cu-N	83.3 (2)
N-Cu-O(6)	95.9 (2)	Cu-O(1)-C(1)	117.2 (4)
(b) In the Ligand			
C(1)-O(1)	1.284 (8)	O(1)-C(1)-O(2)	123.4 (5)
C(1)-O(2)	1.229 (6)	O(1)-C(1)-C(2)	117.2 (5)
C(1)-C(2)	1.525 (9)	O(2)-C(1)-C(2)	119.4 (5)
N-C(2)	1.481 (7)	C(1)-C(2)-N	107.8 (5)
N-S	1.584 (5)	C(2)-N-S	112.6 (4)
S-O(3)	1.457 (5)	N-S-C(3)	110.5 (3)
S-O(4)	1.461 (4)	N-S-O(3)	110.6 (2)
S-C(3)	1.759 (6)	N-S-O(4)	108.0 (2)
		O(3)-S-C(3)	105.7 (3)
		O(4)-S-C(3)	105.8 (2)
		O(4)-S-O(3)	116.0 (2)
		S-C(3)-C(4)	122.1 (5)
		S-C(3)-C(9)	119.1 (5)

(13) This compound, which presents some interesting characteristics, as an anomalous magnetic moment, is under investigation.

(14) Very broad EPR, infrared, and electronic bands do not permit a reasonable assignment of its stereochemistry.

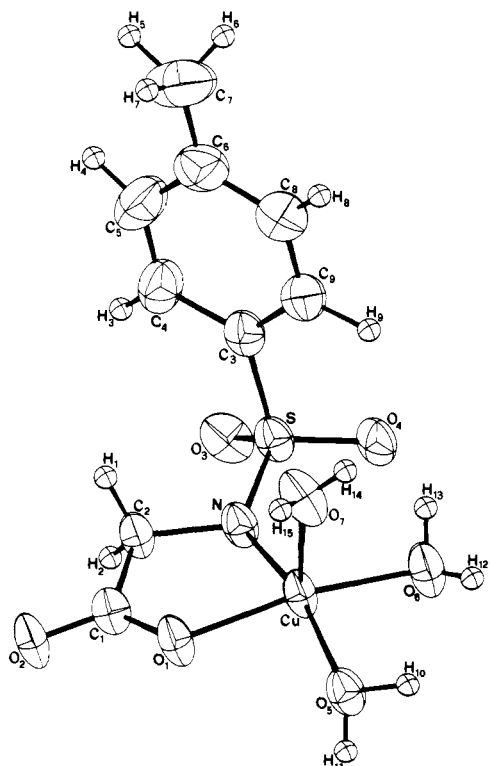


Figure 2. ORTEP view of the $[\text{Cu}(\text{Tsgly})(\text{H}_2\text{O})_3]$ complex showing the atom numbering and the thermal motion ellipsoids (40%) for the nonhydrogen atoms. The hydrogen atoms are represented as spheres of arbitrary radius.

structure with atom numbering. The Cu–N 1.964 (6) Å and Cu–O(carboxylate) 1.931 (4) Å distances are in agreement with those previously found in Cu–amino acid complexes^{15–18} and Cu–O(water) equatorial bond lengths are comparable with that found in bis(*N*-acetyl- β -alaninato)diaquacopper(II),^{6k} while the Cu–O(7) distance (2.259 (4) Å) is comparable with Cu–water (apical) in Cu(II) complexes exhibiting water molecules at the apical position in a pyramidal coordination.^{6k}

The structure of the blue $\text{K}_2[\text{Cu}(\text{Tsgly})_2]$ compound consists of potassium cations and $[\text{CuL}_2]^{2-}$ anions, in which the copper atom is surrounded by two carboxylic oxygens and two deprotonated amide nitrogens of two independent ligand molecules. The coordination geometry can be described as tetrahedrally distorted square-planar. An additional weak interaction (2.717 (3) Å) with the sulfonic oxygen atom from a neighboring ligand ($\text{O}(4)^i$, $i = 1 - x, 1 - y, z$) completes the coordination to $4 + 1$ terms, with an intermediate geometry between square pyramidal and trigonal bipyramidal. In this way the structure of the anion appears as formed by $[\text{Cu}_2\text{L}_4]^{4-}$ dimeric units (Figure 3).

The coordination polyhedron distortion can be described with the distances of each atom from the theoretical coordination plane, N(1)O(1)N(2)O(5) (O(1) 0.156 Å, N(1) –0.243 Å, N(2) –0.242 Å, O(5) 0.155 Å).

The Cu–O(carboxylic) and Cu–N distances (Table V) are comparable with those found in the above described $[\text{Cu}(\text{Tsgly})(\text{H}_2\text{O})_3]$ complex.

The two five-membered chelation rings, O(1)C(1)C(2)N(1)Cu and O(5)C(10)C(11)N(2)Cu, form a dihedral angle of 17.8 (1)°.

The conformation of the chelation rings is quite similar, the torsion angles around the –C–C– bonds, quoted in the Supple-

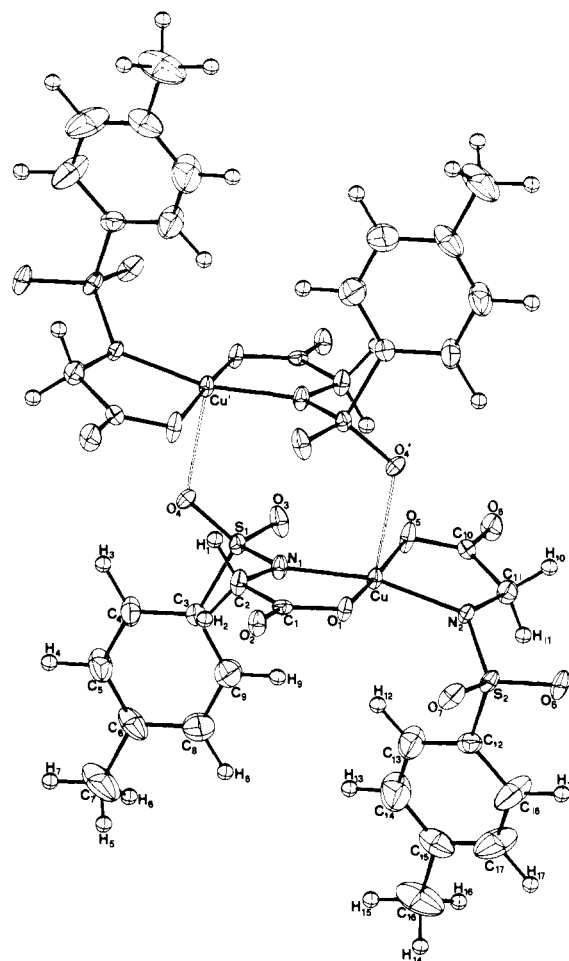


Figure 3. ORTEP view of the $\text{K}_2[\text{Cu}(\text{Tsgly})_2]$ complex showing the atom numbering and the thermal motion ellipsoids (40%) for the nonhydrogen atoms. The hydrogen atoms are represented as spheres of arbitrary radius.

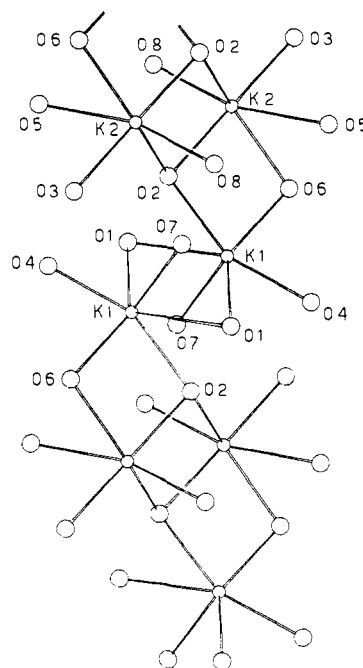


Figure 4. Environment of the potassium ions.

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mentary Material, being very similar.

Each potassium ion (Figure 4 and Table V) is surrounded within 3.0 Å by six oxygen atoms belonging to centrosymmetric mole-

Table V. Bond Distances (Å) and Angles (deg) with esd's in Parentheses for the $K_2[Cu(Tsgly)_2]$ Complex^a

(a) In the Coordination Polyhedron			
Cu-O(1)	1.954 (4)	Cu-O(5)	1.923 (4)
Cu-N(1)	1.969 (7)	Cu-N(2)	2.002 (7)
Cu-O(4) ⁱ	2.717 (5)	O(1)-Cu-O(5)	171.9 (4)
O(1)-Cu-N(1)	83.5 (3)	N(2)-Cu-O(4) ⁱ	97.2 (4)
O(1)-Cu-N(2)	96.3 (3)	O(5)-Cu-O(4) ⁱ	90.6 (3)
N(1)-Cu-O(5)	98.5 (3)	N(1)-Cu-O(4) ⁱ	97.7 (4)
N(2)-Cu-O(5)	83.9 (3)	O(1)-Cu-O(4) ⁱ	81.3 (3)
N(1)-Cu-N(2)	164.9 (4)		
(b) In the Ligands			
C(1)-O(1)	1.287 (9)	C(10)-O(5)	1.283 (9)
C(1)-O(2)	1.230 (7)	C(10)-O(6)	1.232 (7)
C(1)-C(2)	1.522 (12)	C(10)-C(11)	1.508 (12)
C(2)-N(1)	1.468 (7)	C(11)-N(2)	1.502 (8)
N(1)-S(1)	1.571 (7)	N(2)-S(2)	1.570 (6)
S(1)-O(3)	1.447 (4)	S(2)-O(7)	1.443 (4)
S(1)-O(4)	1.455 (6)	S(2)-O(8)	1.450 (8)
S(1)-C(3)	1.783 (7)	S(2)-C(12)	1.783 (8)
Cu-O(1)-C(1)	116.6 (4)	Cu-O(5)-C(10)	117.8 (4)
O(1)-C(1)-O(2)	123.4 (7)	O(5)-C(10)-O(6)	122.4 (7)
O(1)-C(1)-C(2)	117.0 (6)	O(5)-C(10)-C(11)	117.5 (6)
O(2)-C(1)-C(2)	119.6 (6)	O(6)-C(10)-C(11)	120.1 (7)
C(1)-C(2)-N(1)	109.6 (6)	C(10)-C(11)-N(2)	109.8 (6)
C(2)-N(1)-S(1)	112.3 (5)	C(11)-N(2)-S(2)	112.2 (5)
N(1)-S(1)-C(3)	107.4 (3)	N(2)-S(2)-C(12)	108.2 (3)
N(1)-S(1)-O(3)	110.8 (3)	N(2)-S(2)-O(7)	109.2 (3)
N(1)-S(1)-O(4)	111.5 (3)	N(2)-S(2)-O(8)	112.1 (3)
O(3)-S(1)-C(3)	106.0 (3)	O(7)-S(2)-C(12)	106.4 (3)
O(4)-S(1)-C(3)	105.2 (3)	O(8)-S(2)-C(12)	105.0 (3)
O(4)-S(1)-O(3)	115.5 (3)	O(8)-S(2)-O(7)	115.4 (3)
S(1)-C(3)-C(4)	120.5 (6)	S(2)-C(12)-C(13)	121.4 (7)
S(1)-C(3)-C(9)	120.7 (7)	S(2)-C(12)-C(18)	120.6 (7)
(c) In the Potassium Environment			
K(1)-O(1)	2.896 (6)	K(2)-O(8)	2.737 (7)
K(1)-O(6) ⁱⁱ	2.679 (5)	K(2)-O(2) ^{iv}	2.730 (4)
K(1)-O(1) ⁱⁱⁱ	2.892 (4)	K(2)-O(3) ^v	2.670 (4)
K(1)-O(2) ⁱⁱⁱ	2.831 (6)	K(2)-O(5) ^v	2.823 (5)
K(1)-O(7) ⁱⁱⁱ	2.774 (5)	K(2)-O(6) ^v	2.846 (6)
K(1)-O(4)	2.719 (6)	K(2)-O(2) ⁱⁱⁱ	2.784 (5)

^a i = 1 - x, 1 - y, \bar{z} ; ii = \bar{x} , 1 - y, \bar{z} ; iii = 1 - x, \bar{y} , \bar{z} ; iv = x - 1, y, z, v = x, y - 1, z.

Table VI. Contacts Less Than 3.5 Å for $K_2[Cu(Tsgly)_2]$ ^a

O(6)-O(4) ^{iv}	3.471 (6)	O(3)-O(7) ^{vii}	3.456 (8)
C(11)-C(4) ^{iv}	3.453 (8)	C(8)-C(8) ^{viii}	3.361 (12)
O(6)-O(2) ^{vi}	3.471 (6)		

^a iv = x - 1, y, z; vi = x - 1, 1 + y, z; vii = x, 1 + y, z; viii = 1 - x, 1 - y, 1 - z.

cules. These K-O distances correspond to the sums of the ionic radii (2.73 Å), ranging from 2.670 to 2.896 Å. The K(1) is moreover involved in two larger contacts with N(2) (3.133 (6) Å) and with O(7) (3.153 (5) Å). The K(1) and K(2) ions are bridged by carboxylic oxygens in infinite chains running along the [100] axis. In this way, packing (Figure 5) can be considered as mainly determined by the behavior of the potassium ions and completed by van der Waals (Table VI) interactions among the nonpolar side chains of the ligand molecules.

In the $[Cu(Tsgly)(H_2O)_3]$ complex the packing (Figure 6) is determined by a network of hydrogen bonds involving water molecules, carboxylic oxygen, and tosylate oxygen atoms (Table VII). In both complexes layers formed by hydrophobic regions of the amino acid molecules along the [100] and [001] axes for $[Cu(Tsgly)(H_2O)_3]$ and $K_2[Cu(Tsgly)_2]$ complexes, respectively, perpendicular to the hydrophilic regions of the ligand, can be observed. This kind of arrangement of the ligand is normal for metal complexes with amino acids containing nonpolar side chains.

In the three tosylate moieties for the two complexes, bond distances and angles are very similar and in agreement with those observed in other sulfonic derivatives,^{19,22} while the S-N bonds (1.570-1.580 Å) are shorter than those found in uncoordinated

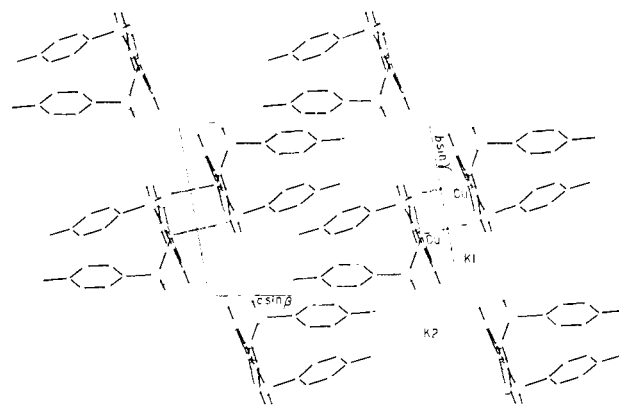


Figure 5. Projection of the structure along [100] the axis.

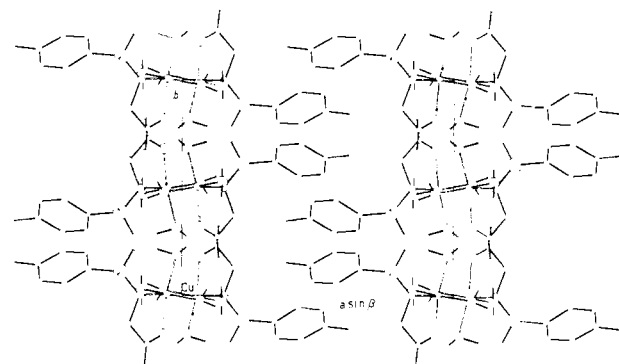


Figure 6. Projection of the structure along the [001] axis.

sulfonamides in which the S-N distance ranges from 1.606 to 1.65 Å.¹⁹⁻²²

Magnetic and Spectroscopic Results. The room-temperature solid magnetic moments of the complexes (Table VIII) are "normal" and typical of "magnetically dilute" complexes,²³ except for that of blue form of $K_2[Cu(Tsgly)_2]$, which may indicate the presence of some type of exchange interaction between the two copper(II) ions in the dimer.

The polycrystalline EPR spectra of all complexes (Table VIII) are of the axial type, suggesting an essentially $d_{x^2-y^2}$ ground state, and show g_{\parallel} values consistent with the presence of different chromophores. For the $K_2[Cu(Tsgly)_2]$ complexes, the g_{\parallel} value in the violet form lower than that in the blue form (chromophore CuO_3N_2 , see structural results) suggests a CuO_2N_2 chromophore, since in the copper(II) complexes g values decrease as the planar ligand field becomes stronger.^{24,25}

For the $Cu(TsglyH)_2 \cdot 4H_2O$ complex, the g_{\parallel} value higher than that of the $[Cu(Tsgly)(H_2O)_3]$ complex (CuO_4N chromophore)^{25,27} is consistent with a chromophore containing only oxygen atoms,^{25,26} which means that the nitrogen atom ligand cannot be involved in the metal ion coordination.

Since square-pyramidal CuN_5 chromophore absorbs at 17700³⁶

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Table VII. Possible Hydrogen Bonding Distances (Å) and Angles (deg) for the [Cu(Tsgly)(H₂O)₃] Complex^a

O(5)···O(2) ⁱ	2.675 (7)	O(5)–H(10)	1.02 (8)	H(10)···O(2) ⁱ	1.65 (9)	O(5)–H(10)···O(2) ⁱ	175
O(5)···O(3) ⁱⁱ	2.766 (6)	O(5)–H(11)	0.92 (6)	H(11)···O(3) ⁱⁱ	1.86 (6)	O(5)–H(11)···O(3) ⁱⁱ	168
O(6)···O(1) ^j	2.639 (7)	O(6)–H(12)	0.79 (10)	H(12)···O(1) ^j	1.86 (9)	O(6)–H(12)···O(1) ^j	172
O(6)···O(4)	2.665 (8)	O(6)–H(13)	0.89 (8)	H(13)···O(4)	2.11 (10)	O(6)–H(13)···O(4)	120
O(7)···O(4) ⁱⁱⁱ	2.863 (5)	O(7)–H(14)	0.80 (9)	H(14)···O(4) ⁱⁱⁱ	2.07 (9)	O(7)–H(14)···O(4) ⁱⁱⁱ	170
O(7)···O(2) ^{iv}	2.886 (6)	O(7)–H(15)	0.78 (8)	H(15)···O(2) ^{iv}	2.11 (9)	O(7)–H(15)···O(2) ^{iv}	177

^a i = $\bar{x}, y - 1/2, 1/2 - z$; ii = $\bar{x}, \bar{y}, \bar{z}$; iii = $x, -y - 1/2, 1/2 + z$; iv = $x, 1/2 - y, 1/2 + z$.

Table VIII. Room-Temperature Magnetic (μ_B) and Spectroscopic (cm⁻¹) Results for the Solid Compounds

	TsglyH ₂	KTsglyH	Cu(TsglyH) ₂ ·4H ₂ O	[Cu(Tsgly)·(H ₂ O) ₃]	K ₂ Cu(Tsgly) ₂		
					blue	violet	
μ_{eff}			1.83	1.86	1.75	1.85	
g_{\parallel}			2.388	2.308	2.231	2.201	
g_{\perp}			2.065	2.078	2.063	2.052	
d–d _{trans}			(10000 sh) 14410	13990	15150	14700 sh 16390 19200	
				CuO _x	CuNO ₄	CuN ₂ O ₃	CuN ₂ O ₂
$\nu(\text{NH})$	3270 s	3410 ms	3270 ms				
$\nu(\text{OCO})_{\text{asym}}$	1718 vs	1615 vs	1590 vs	1615 vs	1605 vs	1630 vs	
$\nu(\text{OCO})_{\text{sym}}$	1230 vs	1375 vs	1408 vs	1395 vs	1390 vs	1365 vs	
$\Delta\nu^a$	488	240	182	220	215	265	
$\nu(\text{SO}_2)_{\text{asym}}$	1335 vs	1320 vs	1328, 1313 vs	1245 vs	1268 vs	1265 vs	
$\nu(\text{SO}_2)_{\text{sym}}$	1155 vs	1158 vs	1158 vs	1132, 1113 vs	1140 vs 1105 vs	1145 vs 1108 vs	
$\nu(\text{SN})$	890 ms	902 ms	902 ms	978 s	982 vs 954 s 938 s 927 ms	958 s 935 s	
$\delta(\text{SO}_2)$	550 m	552 m	563 s	588 s	575 vs	575 vs	
$\rho(\text{SO}_2)$	532 ms	530 in	542 s	550 ms	548 s	547 s	

^a $\Delta\nu = \nu(\text{OCO})_{\text{asym}} - \nu(\text{OCO})_{\text{sym}}$.

or 17 400 cm⁻¹³⁷ and CuO₃N₂ and CuO₄N chromophores at 15 150 cm⁻¹ (in K₂[Cu(Tsgly)₂], blue form) and 13 990 cm⁻¹ (in [Cu(Tsgly)(H₂O)₃]) (see Table VIII), a CuO₅ chromophore may be expected to present a maximum at lower energy than 13 990 cm⁻¹. Therefore, for the Cu(TsglyH)₂·4H₂O complex, which shows a band maximum at 14 410 cm⁻¹, it seems reasonable to suggest the presence of a tetragonal copper(II)–oxygen system.^{28,38}

The IR spectrum of Cu(TsglyH)₂·4H₂O (Table VIII), very similar in band shape and position to those found for the alkali salts of the ligand, confirms a coordination of the *N*-tosylglycine only through the carboxylate group. This type of coordination, normally found in the *N*-protected amino acids investigated up until now,^{5,6} is confirmed by the first structural data performed on its 4-methylpyridine adduct.²⁹

The difference in the electronic spectra between the blue and violet forms (Table VIII) in agreement with the EPR results may be associated with a change from square-pyramidal to square-planar geometry, as decreasing axial interactions result in an increasing d–d transition energy.³⁹ The presence of several forms of amino acid–copper(II) complexes is not unusual, as in the case of bis(tyrosinato)copper(II) complexes, in which differences in

the diffuse reflectance spectra between the blue form, absorbing at 16 000 cm⁻¹, and the mauve form, absorbing at 17 850, 18 850 (sh), and 20 000 cm⁻¹, are attributed to a coordination number and geometry change from trans hexacoordinate (blue form) to four coordinate (mauve form) structure.⁴

The IR spectra of the [Cu(Tsgly)(H₂O)₃] and K₂[Cu(Tsgly)₂] complexes are very different from those of the *N*-tosylglycine, its alkali salts, and the Cu(TsglyH)₂·4H₂O complex in the NH and sulfonyl group spectral regions;^{30–35} this is consistent with the presence of deprotonated nitrogen atom coordinated with the copper(II) ion.

The main conclusions from this work are as follows: (1) The *N*-tosylglycine, when the NH group is not deprotonated (pH < 5), coordinating only through the carboxylate group, acts as a simple carboxylic acid and is therefore a weak ligand for the copper(II) ion. The weak ligand field of the in-plane donor strengthening the axial interactions could favor a tetragonal coordination of the copper(II) ion. (2) The deprotonation of the NH group (at pH > 5, lower than that expected from its pK_A value (see next paper), in agreement with the deprotonation behavior of the peptidic nitrogen atom)¹² accompanied by the coordination of the nitrogen atom produces stable five-membered chelate rings. This favors the five-coordination, since the strong ligand field of the in-plane donor weakens the axial interactions.

Acknowledgment. The authors are grateful to the Centro Strumenti dell'Università di Modena for the recording of the infrared spectra.

Registry No. Cu(TsglyH)₂·4H₂O, 85337-91-3; [Cu(Tsgly)(H₂O)₃], 85337-92-4; K₂[Cu(Tsgly)₂] (violet form), 85404-46-2; K₂[Cu(Tsgly)₂] (blue form), 85337-93-5.

Supplementary Material Available: A listing of thermal parameters, selected least-squares planes, distances involving hydrogen atoms, bond distances and angles in tosylate benzene rings, torsion angles, and final structure factors (31 pages). Ordering information is given on any current masthead page.

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