the IR bands at 1650–1700 cm^{-1} observed in the spectra of the oxidation products are probably indicative of the formation of carbonyl groups. Products containing these functions have been shown to result from oxidation of the ligand by reaction of metal complexes with dioxygen.[53] It is important to note that the products that result from the irreversible oxygenation of [Cu(L-bisp)]$^+$ are different, as the ester and imino groups of the ligand are unaffected. It is possible that in the Cu reaction the ligand undergoes simple hydroxylation, apparently a common route for the evolution of many Cu(I) + O_2 systems. The L-bisp ligand appears to provide some stabilization for simple copper–dioxygen and cobalt–dioxygen species formed at the early stages of the oxygenation. We are currently trying to characterize these species.

Acknowledgment. This work was supported by the Italian MPI and by the U.S. National Institutes of Health (Grant No. HL 13157). We thank the Italian CNR for instrumentation facilities, M. Bonfa for recording the NMR spectra, P. Russo for the MS spectra measurements, and M. S. Franzoni for the magnetic susceptibility measurements.

Registry No. [Cu(L-bisp)][ClO_4], 89196-41-8; [Zn(L-bisp)][ClO_4]$_2$, 89178-90-5; [Cu(L-bisp)][ClO_4]$_2$, 89178-92-7; [Co(L-bisp)][ClO_4]$_2$, 89178-94-9; [Fe(L-bisp)][ClO_4]$_2$, 89178-96-1; O_2, 7782-44-7; L-histidine methyl ester, 1499-46-3; 2,6-diacetylpyridine, 1129-30-2.

Supplementary Material Available: Listings of thermal parameters for the non-hydrogen atoms (Table III), idealized hydrogen positions (Table IV), observed and calculated structure amplitudes (Table V), bond distances and angles in the coordination sphere (Table VI), and least-squares planes (Table VII) and circular dichroism spectra of [Co(L-bisp)][ClO_4]$_2$ in degassed pyridine at different times (Figure 5), proton NMR spectra of [Cu(L-bisp)][ClO_4] in degassed CD_3CN (Figure 6) and [Zn(L-bisp)][ClO_4]$_2$ in CD_3CN (Figure 7), and electronic spectra in the oxygenation of [Fe(L-bisp)][ClO_4]$_2$ (Figure 11) (29 pages). Ordering information is given on any current masthead page.

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Contribution from the Ministero della Pubblica Istruzione of Italy,
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Coordination Behavior of 4-Toluenesulfonamide Derivatives: Thermal and Spectroscopic Properties of (*N*-Tosylglycinato)(2,2′-bipyridine)copper(II) Complexes. Crystal and Molecular Structure of (Ethanol)(*N*-tosylglycinato)(2,2′-bipyridine)copper(II)

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The compounds of formula [Cu(Tsgly)(bpy)L] and anhydrous [Cu(Tsgly)(bpy)] (Tsgly = *N*–tosylglycinate dianion; bpy = 2,2′-bipyridine; L = EtOH, H_2O) were synthesized and characterized by means of thermogravimetric, electronic, infrared, and EPR spectra. For one of them, the [Cu(Tsgly)(bpy)(EtOH)] complex, the crystal structure was also determined. The compound crystallizes in the monoclinic space group $P2_1/n$ with 4 formula units in a cell of dimensions $a = 9.677$ (1) Å, $b = 10.460$ (1) Å, $c = 21.488$ (2) Å, and $\beta = 98.27$ (1)°. The structure was solved by the heavy-atom method and refined by least-squares calculations to $R = 0.039$ for 1705 observed reflections. The structure consists of discrete molecular units of [Cu(Tsgly)(bpy)(EtOH)]. The Cu atom shows tetrahedrally distorted square-pyramidal N_3O_2 coordination. The Tsgly dianion and the bpy molecule act as bidentate ligands in the equatorial plane, and the ethanol is bonded to the metal atom in the apical position. The thermogravimetric, EPR, and electronic results for the aquo and ethanol derivatives suggest that the stability of the in-plane ligands permits successive substitution reactions at the apical position. The infrared spectra for the aquo and ethanol adducts are consistent with the presence of a coordinated water or ethanol molecule.

Introduction

Investigation of the Cu(II)–*N*-tosylglycinate system in the solid state and in solution (aqueous and ethanolic)[2] has pointed out, on the one hand, the differences in the coordination behavior of this *N*-tosyl derivative with respect to that of *N*-acetyl and *N*-benzoyl ones[3] and, on the other hand, some meaningful similarities with the pH-dependent coordination behavior of oligoglycines.[4] In fact in these peptides and in *N*-tosylglycine,[2,4] contrary to *N*-acetyl and *N*-benzoyl derivatives,[3] the presence of the Cu(II) ion enables the deprotonation of the peptide or sulfonamide nitrogen atom. As a consequence, the *N*-tosylglycine may act as a bidentate ligand through a carboxylic oxygen atom and the deprotonated sulfonamide nitrogen atom, forming a very stable five-membered chelate ring. In fact at pH $\geq$ 5 it separates the complex [Cu(Tsgly)(H_2O)$_3$] where the copper(II) ion is in a square-pyramidal arrangement.[2a] As this aquo complex contains three coordinated water molecules,[2a] it must easily react with nitrogen donor ligands. Therefore, in this paper we report the structural, spectroscopic, and thermogravimetric results on the ternary complexes obtained by reaction of [Cu(Tsgly)(H_2O)$_3$] with bpy (2,2′-bipyridine) in ethanolic and aqueous solution with the aim of

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(1) To whom correspondence should be addressed.

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Table I. Summary of Crystal Data Collection

diffractometer	Philips PW 1100
radiation	graphite-monochromated Cu Kα (λ = 1.541 78 Å)
temp, °C	20 ± 2
cryst system	monoclinic
space group	$P2_1/n$ (C_2^5h, No. 14)
a, Å	9.677 (1)
b, Å	10.460 (1)
c, Å	21.488 (2)
β, deg	98.27 (1)
V, Å^3	2152.5
mol formula	$C_{21}H_{23}CuN_3O_5S$
mol wt	492.81
Z	4
$F(000)$	1019.9
ρ(calcd), g cm^{-3}	1.52
ρ(obsd), g cm^{-3}	1.50 (by flotation)
reflcns measd	$\pm h,k,l$
scan type	$\omega-2\theta$
θ range, deg	2–60
scan speed, deg min^{-1}	2.1
scan width, deg	1.1
bkgd time, s	10 at beginning and end of the scan
stds	1 every 50 reflcns (no changes)
colled reflcns	3496
obsd reflcns	1705 with $I > 2.0\sigma(I)$ [$\sigma(I)$ = (peak counts + total bkgd counts)$^{1/2}$]
cryst size, mm	~0.16 × 0.10 × 0.07
abs coeff, cm^{-1}	25.0
abs cor	not applied

clarifying the mutual influence of the potentially active ligands present in these systems.

Furthermore, as *N*-tosylglycine may be considered as a 4-toluenesulfonamide derivative, our results may be helpful in understanding the coordination behavior, still as yet controversial, of this important class of compounds.[2f,5]

Experimental Section

All chemicals were reagent grade and used as received.

Preparation of (Ethanol)(*N*-tosylglycinato)(2,2′-bipyridine)copper(II) and Aqua(*N*-tosylglycinato)(2,2′-bipyridine)copper(II), [Cu(Tsgly)(bpy)(EtOH)] and [Cu(Tsgly)(bpy)(H_2O)]. The solid bpy was added alternately to an ethanolic or aqueous solution of [Cu(Tsgly)(H_2O)$_3$] complex until deep blue solutions were reached. When these solutions were evaporated at room temperature (20 °C), after 12 h, dark blue crystals separated. These compounds can be transformed from one into another by stirring for 1 h the solid [Cu(Tsgly)(bpy)L] (L = EtOH, H_2O) in a water–ethanol (5:1 or 1:5) solution.

[Cu(Tsgly)(bpy)(EtOH)]: Anal. Calcd for $C_{21}H_{23}CuN_3O_5S$: C, 51.13; H, 4.70; N, 8.53; S, 6.51; EtOH, 9.34. Found: C, 51.16; H, 4.73; N, 8.49; S, 6.33; EtOH, 9.60.

[Cu(Tsgly)(bpy)(H_2O)]: Anal. Calcd for $C_{19}H_{19}CuN_3O_5S$: C, 49.05; H, 4.12; N, 9.04; S, 6.90; H_2O, 3.88. Found: C, 48.81; H, 4.22; N, 8.91; S, 6.63; H_2O, 3.92.

Preparation of (*N*-Tosylglycinato)(2,2′-bipyridine)copper(II), [Cu(Tsgly)(bpy)]. This blue-green compound was obtained by allowing the solid [Cu(Tsgly)(bpy)(EtOH)] to stand in air at 30 °C for several weeks or by complete evaporation at 50 °C of an ethanolic solution of [Cu(Tsgly)(H_2O)$_3$] and bpy in a molar ratio of 1:1.

Anal. Calcd for $C_{19}H_{17}CuN_3O_4S$: C, 51.03; H, 3.84; N, 9.41; S, 7.18. Found: C, 50.93; H, 3.83; N, 9.53; S, 7.03.

Only crystals of [Cu(Tsgly)(bpy)(EtOH)] were found suitable for X-ray structural analysis.

Physical Measurements. The electronic, EPR, and infrared spectra were performed on the solid complexes as described in ref 2a. The thermogravimetric analysis was performed at a speed rate of 5 °C/min with a Mettler TA3000 instrument.

Table II. Atomic Coordinates with Esd's in Parentheses

atom	x	y	z
Cu	0.5455 (1)	0.3824 (1)	0.2631 (1)
N(1)	0.7041 (5)	0.3802 (5)	0.3336 (2)
C(1)	0.7601 (7)	0.2761 (6)	0.3636 (3)
C(2)	0.8691 (8)	0.2818 (7)	0.4116 (3)
C(3)	0.9229 (8)	0.3993 (8)	0.4296 (3)
C(4)	0.8692 (8)	0.5074 (7)	0.3984 (3)
C(5)	0.7578 (7)	0.4963 (6)	0.3508 (3)
N(2)	0.5838 (5)	0.5703 (4)	0.2697 (2)
C(6)	0.5056 (7)	0.6616 (6)	0.2384 (3)
C(7)	0.5266 (7)	0.7899 (6)	0.2516 (3)
C(8)	0.6350 (8)	0.8234 (6)	0.2975 (3)
C(9)	0.7153 (7)	0.7314 (6)	0.3305 (3)
C(10)	0.6851 (6)	0.6035 (6)	0.3159 (3)
O(1)	0.5157 (4)	0.1996 (4)	0.2686 (2)
O(2)	0.3567 (5)	0.0528 (4)	0.2381 (2)
C(11)	0.4070 (6)	0.1602 (5)	0.2344 (3)
C(12)	0.3339 (7)	0.2538 (6)	0.1862 (3)
N(3)	0.4215 (5)	0.3679 (5)	0.1836 (2)
S	0.4551 (2)	0.4087 (1)	0.1176 (1)
O(3)	0.4651 (5)	0.3014 (4)	0.0754 (2)
O(4)	0.5756 (4)	0.4917 (4)	0.1266 (2)
C(13)	0.3120 (6)	0.5004 (5)	0.0816 (3)
C(14)	0.3075 (7)	0.5332 (7)	0.0185 (3)
C(15)	0.1963 (7)	0.6046 (8)	−0.0102 (3)
C(16)	0.0900 (7)	0.6437 (6)	0.0209 (3)
C(17)	0.0967 (7)	0.6093 (7)	0.0827 (3)
C(18)	0.2080 (7)	0.5382 (6)	0.1132 (3)
C(19)	−0.0316 (8)	0.7208 (8)	−0.0114 (4)
O(5)	0.3602 (5)	0.4239 (5)	0.3222 (2)
C(20)	0.3838 (10)	0.4643 (10)	0.3853 (4)
C(21)	0.2694 (13)	0.4532 (14)	0.4222 (6)

X-ray Data Collection. The crystal, sealed on a glass fiber, was transferred in a random orientation to a Philips PW 1100 automated four-circle diffractometer. Accurate cell constants were derived from a least-squares refinement of the setting angles of 20 reflections. Intensity data were then collected under the conditions listed in Table I.

A survey of the complete data set revealed systematic absences compatible only with space group $P2_1/n$. The intensities were corrected for Lorentz and polarization effects but not for absorption in view of the small crystal dimensions. Only the observed reflections, placed on an (approximately) absolute scale by means of a Wilson plot, were used in the structure analysis.

Solution and Refinement of the Structure. The structure was solved by conventional heavy-atom methods and refined by full-matrix least-squares techniques.[6] All non-hydrogen atoms were treated anisotropically, and all hydrogen atoms were added to the model as fixed contributors at their observed positions, except for those of the C(21) methyl group, which were placed in calculated positions staggered with respect to the adjacent methylene group. R and R_w converged to their final values of 0.039 and 0.042, respectively, with changes in parameters in the last least-squares cycle being less than 0.10 of their esd's. A final difference map had no significant feature, with no peaks higher than 0.35 e Å^{-3}. Unit weights were used at all stages; no trends of $\sum w(|F_o| - |F_c|)^2$ vs. $|F_o|$, sin θ, or Miller indices were observed, and the weighting scheme was better than that based on $\sigma(F)$ values previously tested. During refinement, zero weight was assigned to two strong low-order reflections, which may be affected by secondary extinction.

Complex neutral-atom scattering factors[7] were employed throughout; major calculations were carried out on a CDC Cyber 7600 computer by using the SHELX-76 program package[8] and the ORTEP plotting program.[9]

Final fractional coordinates for non-hydrogen atoms are listed in Table II. Anisotropic temperature factors, hydrogen atom parameters,

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(5) Sigel, H.; Martin, R. B. *Chem. Rev.* **1982**, *82*, 385 and references cited therein.

(6) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is the weighting factor. The unweighted and weighted residuals are $R = (\sum||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

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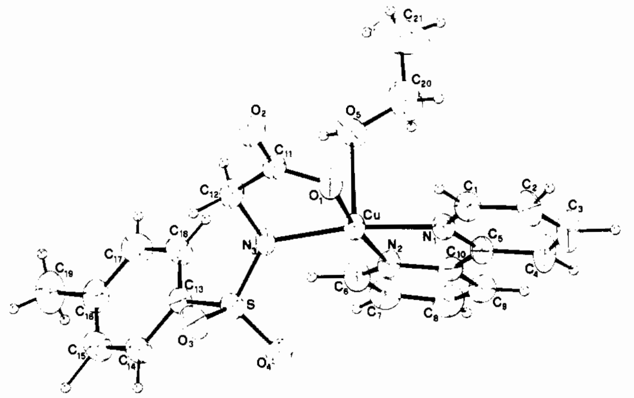

Figure 1. ORTEP view of the [Cu(Tsgly)(bpy)(EtOH)] complex showing the labeling scheme and atomic vibrational ellipsoids (40%). The hydrogen atoms are shown as spheres of arbitrary radius.

Table III. Selected Bond Distances (Å) and Bond Angles (deg) with Esd's in Parentheses

Distances			
Cu-N(1)	1.996 (5)	O(1)-C(11)	1.263 (7)
Cu-N(2)	2.001 (5)	O(2)-C(11)	1.232 (6)
Cu-O(1)	1.940 (4)	C(12)-N(3)	1.470 (7)
Cu-N(3)	1.946 (4)	N(3)-S	1.559 (5)
Cu-O(5)	2.382 (4)	S-O(3)	1.455 (4)
N(1)-C(1)	1.340 (7)	S-O(4)	1.444 (4)
N(1)-C(5)	1.352 (7)	S-C(13)	1.768 (6)
N(2)-C(6)	1.339 (7)	O(5)-C(20)	1.408 (9)
N(2)-C(10)	1.337 (7)		

Angles			
N(1)-Cu-N(2)	81.0 (2)	C(5)-N(1)-C(1)	119.1 (5)
N(1)-Cu-O(1)	92.7 (2)	N(1)-C(5)-C(10)	114.1 (5)
N(1)-Cu-N(3)	167.1 (2)	C(10)-N(2)-C(6)	119.3 (5)
N(1)-Cu-O(5)	98.8 (2)	C(9)-C(10)-N(2)	121.6 (6)
N(2)-Cu-O(1)	172.4 (2)	O(1)-C(11)-O(2)	124.3 (5)
N(2)-Cu-N(3)	102.9 (2)	O(1)-C(11)-C(12)	117.0 (5)
N(2)-Cu-O(5)	85.9 (2)	O(2)-C(11)-C(12)	118.8 (5)
O(1)-Cu-N(3)	84.2 (2)	C(11)-C(12)-N(3)	109.5 (5)
O(1)-Cu-O(5)	91.0 (2)	C(12)-N(3)-S	116.9 (4)
N(3)-Cu-O(5)	93.8 (2)	N(3)-S-O(3)	113.5 (3)
Cu-N(1)-C(1)	126.0 (4)	N(3)-S-O(4)	108.2 (2)
Cu-N(1)-C(5)	114.9 (4)	N(3)-S-C(13)	107.0 (3)
Cu-N(2)-C(6)	125.4 (4)	O(3)-S-O(4)	115.0 (3)
Cu-N(2)-C(10)	114.6 (4)	O(3)-S-C(13)	105.3 (3)
Cu-O(1)-C(11)	113.8 (4)	O(4)-S-C(13)	107.4 (3)
Cu-N(3)-C(12)	108.4 (3)	S-C(13)-C(14)	118.2 (5)
Cu-N(3)-S	126.4 (3)	S-C(13)-C(18)	122.2 (5)
Cu-O(5)-C(20)	122.6 (5)	O(5)-C(20)-C(21)	118.0 (9)

and tables of observed and calculated structure factors are available as supplementary material.

Analysis. Nitrogen, carbon, hydrogen, and sulfur were analyzed with a C. Erba Elemental Analyzer Instrument Model 1106 by G. Pistoni. The ethanol and water contents were determined thermogravimetrically.

Results and Discussion

Description of the Structure. A drawing of the structure, showing the labeling scheme, is given in Figure 1 and a stereoview of the unit cell contents in Figure 2. Selected bond distances and bond angles are listed in Table III. Complete bond distances and bond angles and selected least-squares planes are given as supplementary material. For the sake of comparison, a summary of some structural features of previously investigated (*N*-tosylglycinato)copper(II) complexes are reported in Table IV.

The crystal is composed of discrete molecular units of [Cu(Tsgly)(bpy)(EtOH)], linked into linear chains through hydrogen bonds.

Environment of the Copper Atom. The Cu atom exhibits tetrahedrally distorted square-pyramidal N_3O_2 coordination arising from ligation by a Tsgly dianion and a bpy molecule,

Table IV. Summary of Coordination Geometry of (*N*-Tosylglycinato)copper(II) Complexes of Known Structure

compd	coord geom	chromophore	mean $Cu-O_{eq}$ bond length, Å	mean $Cu-N_{eq}$ bond length, Å	$Cu-O_{ax}$ bond length, Å	Tsgly or TsglyH bonding mode	mean N-S bond length, Å	mean S-C bond length, Å	ref
$[Cu(Tsgly)(H_2O)_3]$	square pyramidal	NO_4	1.957 (4)	1.964 (6)	2.259 (4) (water)	bidentate (O, N)	1.584 (5)	1.759 (6)	2a
$K_2[Cu(Tsgly)_2]$	dimeric 4 + 1	N_2O_3	1.938 (4)	1.985 (7)	2.717 (5) (sulfonic)	bidentate (O, N) and O(sulfonic) bridging	1.570 (7)	1.783 (8)	2a
[Cu(Tsgly)(bpy)(EtOH)]	square pyramidal	N_3O_2	1.940 (4)	1.981 (5)	2.382 (4) (ethanolic)	bidentate (O, N)	1.559 (5)	1.768 (6)	this work
$[Cu_2(TsglyH)_4]_n$	dimeric cupric acetate type	O_5	1.955 (7)		2.168 (7) (sulfonic)	bidentate (O, O) bridging and O(sulfonic) bridging	1.616 (9)	1.756 (9)	2c
$[Cu(TsglyH)_2(N\text{-MeIm})_2]^a$	square planar	N_2O_2	1.967 (3)	1.970 (4)		unidentate (O)	1.621 (5)	1.758 (5)	2d
$[Cu(TsglyH)_2(4\text{-Mepy})_2{\cdot}H_2O]_n{}^b$	tetragonal bipyramidal	N_2O_4	1.929 (4)	1.977 (5)	2.755 (1) (bridging water)	unidentate (O)	1.596 (5)	1.742 (6)	2c

[a] *N*-MeIm = *N*-methylimidazole. [b] 4-Mepy = 4-methylpyridine.

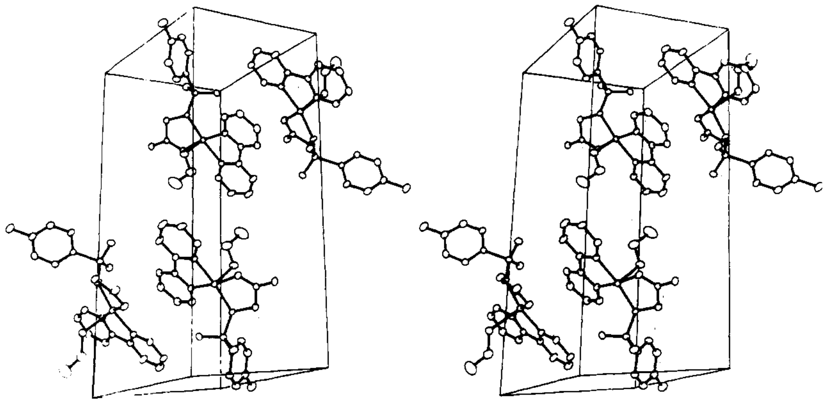

Figure 2. Stereoview of the unit cell contents.

both acting as bidentate ligands in the equatorial plane, and by an ethanolic oxygen in apical position. As a common feature of many Cu(II) small peptide or amino acid complexes,[10-14] the four equatorial donor atoms shown deviations (from −0.142 to 0.141 Å) from their least-squares mean plane in the pattern of a tetrahedral distortion of the approximately planar base; the Cu atom deviates 0.077 Å from the plane toward the apical O atom. The least-squares planes through the five-membered chelate rings make a dihedral angle of 13.6°. A comparison with the structural features of the [Cu(Tsgly)(H_2O)$_3$] and K_2[Cu(Tsgly)$_2$] complexes,[2a] in which the Tsgly dianion similarly acts as a bidentate ligand in the equatorial plane of the square-pyramidal metal atom, shows significant differences within the coordination polyhedra. The four equatorial donor atoms are coplanar in the [Cu(Tsgly)(H_2O)$_3$] salt; the substitution of the two water molecules by the chelating bpy ligand in the copper coordination sphere determines a relevant tetrahedral distortion of the equatorial plane of the [Cu(Tsgly)(bpy)(EtOH)] complex. More relevant deviations, up to 0.243 Å, occur in the basal coordination plane of the K_2[Cu(Tsgly)$_2$] salt, in which the two five-membered glycine-type chelate rings make a dihedral angle of 17.8°. Relevant differences occur also in the Cu–O(apical) bond distances, suggesting a correlation with the tetrahedral distortions of the basal coordination plane, although major contributors could be the chemical nature of the oxygen atoms or crystal packing requirements such as hydrogen bonding. A Cu–O(water) apical distance of 2.259 (4) Å was found for the [Cu(Tsgly)(H_2O)$_3$] salt, while in the K_2[Cu(Tsgly)$_2$] complex a Cu–O(sulfonic) axial interaction of 2.717 (5) Å leads to [Cu_2(Tsgly)$_4$]$^{4-}$ dimeric units. It is interesting to note that the Cu–O(ethanolic) apical distance (2.382 (4) Å) of the present compound compares well with the Cu–O(carboxylate) (2.37 (2) Å) and Cu–O(water) (2.368 (5) Å) axial interactions found in the (L-aspartato)(imidazole)copper(II) dihydrate[13] and in the aqua(L-aspartato)(2,2′-bipyridine)copper(II) trihydrate,[14] respectively; both latter complexes show quite similar tetrahedral distortions of the square-pyramidal coordination polyhedron.

It must also be noted that in the present and in the previously reported copper(II)-*N*-tosylglycinate complexes the mean value of 1.97 Å for the Cu–N(sulfonamide)[2a] bond length is significantly longer that the average value of 1.90 Å found for the Cu–N(peptide) bond.[15] This indicates a coordination ability of N^-(sulfonamide) lower than that of N^-(peptide) as expected because of the electrophilic effect of the $-SO_2-$ group, which is greater than that of the –CO– group.[5]

Table V. Room-Temperature (298 K) Electronic (10^{-3} cm^{-1}) and Infrared (cm^{-1}) and Low-Temperature (123 K) EPR Results, Weight-Loss Temperature Range (K), and Decomposition Temperature (K) for the Complexes

	[Cu(Tsgly)-(bpy)(EtOH)][a]	[Cu(Tsgly)-(bpy)(H_2O)][b]	[Cu(Tsgly)-(bpy)]
weight-loss temp range	381–411	406–428	
dec temp	443	443	453
d-d band max	16.4 14.7	16.7	14.2
$g_\parallel$	2.217	2.202	
$g_\perp$	2.069	2.065	
g_o[c]	2.118	2.111	$g_i = 2.144$
$\nu(OCO)_{as}$	1609 vs	1625 vs	1615 vs
$\nu(OCO)_s$	1375 vs	1365 vs	1380 vs
$\nu(SO_2)_{as}$	1250 vs	1250 vs	1265 vs
$\nu(SO_2)_s$	1135 s, 1120 vs	1130 s, 1105 vs	1135 vs, 1105 vs
ν(SN)	1020 s	1010 s	1018 s

[a] The bands at 3200 m–s b (ν(OH)), 1300 s (ν(OH)), and 1050 s (ν(CO)) are assigned to the coordinated ethanol molecule. [b] The bands at 3530 m–s ($\nu(OH)_{as}$) and 3450 sh ($\nu(OH)_s$) are assigned to the coordinated water molecule. [c] $g_o = [(g_\parallel + 2g_\perp)/3]$.

Furthermore, the replacement of the apical water molecule of the parent [Cu(Tsgly)(H_2O)$_3$] complex from a poor coordinating species such as ethanol suggests both that bpy increases the stability of the equatorial ligands with respect to the parent complex (adding a further reasonable justification to the lengthening of the Cu–O(apical) bond)[16] and that successive substitution at this fifth axial position may take place without affecting the equatorial atoms.

The *N*-Tosylglycinate Dianion. As expected and previously reported,[2a] the sulfonamide deprotonation and the successive replacement of the hydrogen atom with a Cu atom influences some of the internal bond distances of the tosylglycinate dianion, especially the S–N and S–O bonds, which become slightly shorter and longer, respectively, with respect to the complexes of undeprotonated *N*-tosylglycine. This fact, parallelling the behavior of peptides,[4c] may be associated with an increasing of the double-bond character of S–N bond and a slight diminishing of bond order of S–O bonds.

The 2,2′-Bipyridine Ligand. Bond distances and bond angles within the bpy molecule, whose individual pyridine rings are

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planar within ±0.016 Å and twisted by 4.5° about the C(2)–C(2′) bond, are consistent with those previously observed for this coordinated ligand.[17,18]

Hydrogen Bonding. The crystal packing is mainly due to a hydrogen-bond interaction between the alcoholic group and the uncoordinated carboxylate O(2) atom of an adjacent molecular unit [O(5)···O(2)^{i} = 2.668 (6) Å; O(5)–H = 0.88 Å; H···O(2)^{i} = 1.80 Å; O(5)–H···O(2)^{i} = 167.9° (i = $^1/_2 - x$, $^1/_2 + y$, $^1/_2 - z$)]. The resulting linear chains are separated by normal van der Waals distances.

Thermogravimetric and Spectroscopic Results. The thermogravimetric analysis shows a sharp maximum in the 381–411 and 406–428 K temperature ranges, without decomposition (Table V), for the EtOH and H_2O adducts, respectively, corresponding to the complete loss of an ethanol or water molecule. That the temperature for the loss of H_2O is greater than that for the coordinated EtOH molecule strongly supports the hypothesis that the H_2O molecule is also directly involved in copper coordination.

The room-temperature solid-state electronic data and the EPR parameters at 123 K (Table V) of the aquo and the structurally known EtOH derivatives are similar, suggesting the same square-pyramidal geometry with a CuN_3O_2 chromophore for both the complexes.[14,19]

Therefore, the thermal, electronic, and EPR results confirm that the in-plane [Cu(Tsgly)(bpy)] moiety is almost unaffected by the easy replacement of ethanol with a coordinated water molecule in the apical position.

The loss of the apical ligand makes it necessary to rearrange the in-plane ligands by increasing the dihedral angle between the plane of Tsgly and bpy ligands, which gives rise to distorted tetrahedral geometry. This is supported by the shift to 14.2 × 10^3 cm^{-1} (Table V) of the d–d band maximum and the increase of $g_{\parallel}$ in the anhydrous complex with respect to those of alcoholic or aquo complexes.[20,21]

The more relevant infrared bands of our complexes are reported in Table V and are assigned by comparison with those of previously investigated copper complexes containing deprotonated *N*-tosylglycine.[2a] Table V also reports the bands attributable to coordinated ethanol and water molecules and their tentative assignments.

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Registry No. Cu(Tsgly)(bpy)(EtOH), 88769-68-0; Cu(Tsgly)(bpy)(H_2O), 88769-67-9; Cu(Tsgly)(bpy), 88478-86-8; Cu(Tsgly)$(H_2O)_3$, 85337-92-4.

Supplementary Material Available: Listings of least-squares planes, complete bond angles and distances, hydrogen atom positions, anisotropic thermal parameters, and observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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Single-Crystal X-ray and Spectroscopic Studies on the Complex Aquo[tris[(3,5-dimethyl-1-pyrazolyl)methyl]amine]cobalt(II) Perchlorate. A Spectroscopic Model of Cobalt-Substituted Carbonic Anhydrase

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The X-ray structure of the complex aquo[tris[(3,5-dimethyl-1-pyrazolyl)methyl]amine]cobalt(II) perchlorate, [Co(H_2O)(MeTPMA)]$(ClO_4)_2$, has been solved and shown to consist of the five-coordinate [Co(H_2O)(MeTPMA)]$^{2+}$ cation and perchlorate anions. (Crystal data: orthorhombic, space group $Pca2_1$, a = 18.456 (8) Å, b = 13.480 (6) Å, c = 10.888 (6) Å, Z = 4; R = 0.061, 1820 reflections.) The cation shows several similarities with cobalt-substituted carbonic anhydrase. The cation is essentially trigonal bipyramidal with the amino nitrogen and the water molecule in the apical positions. The electronic and EPR spectra have been measured and interpreted in terms of angular-overlap parameters.

Introduction

The complex aquo[tris[(3,5-dimethyl-1-pyrazolyl)methyl]amine]cobalt(II) perchlorate, [Co(H_2O)(MeTPMA)]$(ClO_4)_2$, has been recently reported[1] to be a spectroscopic model for cobalt-substituted carbonic anhydrase (CoCA). The metal ion is coordinated by three pyrazole nitrogens, one amine nitrogen, and a water oxygen. The coordinated water in the model complex has a pK_a of 9.1, which matches with the value of CoCA in the range 6–7.5,[2] depending on the particular isoenzyme. To achieve a better understanding of the system, we have determined the X-ray structure of the above complex and have recorded its single-crystal polarized electronic and EPR spectra. In particular, it appeared interesting to us to understand the ligand field parameters of a single coordinated water molecule and investigate the possible connections with its pK_a value.

Experimental Section

Synthesis of the Complex. The complex [Co(H_2O)(MeTPMA)]$(ClO_4)_2$ was prepared as reported elsewhere.[1] Crystals suitable for X-ray diffraction and polarized electronic spectra were obtained by recrystallization of the complex from ethanol–diethyl ether solutions.

X-ray Data Collection and Reduction for [Co(H_2O)(MeTPMA)]$(ClO_4)_2$. The compound crystallizes in the form of elongated plates. A crystal of dimensions 0.06 × 0.20 × 0.80 mm was used for crystal data and intensity data collection. A Philips PW 1100 automatic diffractometer and graphite-monochromated MoKα radiation (λ = 0.71069 Å) were used for all operations. The lattice constants, determined from the setting angles of 12 pairs of reflections

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