Table III. Spectroscopic Data for Copper(II) in Solvents Containing Chloride Ion

solvent system	*t*, °C	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	ref
47.3 mol % $AlCl_3$–MEIC	25	293 (8652), 407 (2596)	this work
DMF[a] + 2.7 M LiCl	25	295 (5974), 411 (2594)	this work
DMF + 3.0 M MEIC	25	282 (16 503), 292[b] (13 000), 408 (2547)	this work
DMF + 3 M LiCl	25	296 (5060), 411 (2220)	15
Me_2SO[c] + 1 M LiCl	25	294 (5720), 410 (2720)	16
PC[d] + 0.1 M Et_4NCl[e]	25	294 (5840), 410 (2650)	16
LiCl–KCl	367	260 (1520), 370 (680)	12

[a] *N,N*-Dimethylformamide. [b] Shoulder. [c] Dimethyl sulfoxide. [d] Propylene carbonate. [e] Tetraethylammonium chloride.

melt and organic solutions containing lithium chloride, respectively. An absorption spectrum of MEIC dissolved in DMF, without added copper(II), is shown in Figure 5 also. It can be seen that this solution absorbs strongly around 282 nm.

Considered together, the evidence presented above indicates that copper(II) is probably complexed as $CuCl_4^{2-}$ in the 47.3 mol % $AlCl_3$–MEIC melt and in DMF containing MEIC. However, the spectra observed for these solutions are distorted at wavelengths proximate to 295 nm by strong absorption due to the 1-methyl-3-ethylimidazolium cation. In fact, the UV cutoff for the basic $AlCl_3$–MEIC melt is located at about 290 nm. The most compelling evidence for $CuCl_4^{2-}$ is the 407-nm absorption peak. It should be noted that no other mononuclear copper(II) chloro complexes, e.g., $CuCl^+$, $CuCl_2$, or $CuCl_3^-$, are reported to exhibit significant absorption close to this wavelength.[15,16] One possible exception may be $CuCl_5^{3-}$.[20] However, virtually no solution spectroscopy has been reported for this species to allow comparison. It should be noted that copper(II), octahedrally coordinated in molten $AlCl_3$, exhibits an absorption maximum around 862 nm.[13]

Absorptivities for the 407-nm peak in the spectrum of copper(II) in basic $AlCl_3$–MEIC melt were measured as a function of melt composition. The average value obtained was 2474 ± 250 M^{-1} cm^{-1} over the composition range extending from 48.2 to 45.3 mol %. This suggests that $CuCl_4^{2-}$ may be the dominant copper(II) chloro complex in basic $AlCl_3$–MEIC melt over this composition range.

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Registry No. Aluminum chloride, 7446-70-0; 1-methyl-3-ethylimidazolium chloride, 65039-09-0.

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Structure and Spectroscopic Properties of Ternary Complexes of Copper(II) *N*-Tosylglycinates. Crystal and Molecular Structure of *catena*-(μ-Aqua)bis(*N*-tosylglycinato)bis(4-methylpyridine)copper(II). A Case of a Linear-Chain Water-Bridged Copper(II) Polymer

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Two compounds of the type $[Cu(TsglyH)_2X_2{\cdot}H_2O]$ (TsglyH = *N*-tosylglycinate monoanion and X = pyridine (py) and 4-methylpyridine (4-Mepy)) were prepared and characterized by means of magnetic, EPR, electronic, and IR spectra. For one of them, *catena*-(μ-aqua)bis(*N*-tosylglycinato)bis(4-methylpyridine)copper(II), the crystal structure was also determined. The crystals are monoclinic, space group *C*2/*c*, with four molecules in a unit cell of dimensions *a* = 19.089 (10) Å, *b* = 15.891 (5) Å, *c* = 10.883 (3) Å, and β = 100.45 (1)°. The structure was solved by the heavy-atom technique and refined by the full-matrix least-squares method to a final *R* index of 0.047 for 1965 unique reflections. The copper environment consists of two centrosymmetrically related carboxylic oxygens and two 4-methylpyridine nitrogens in a square-planar arrangement. Two centrosymmetric water molecules, lying on the twofold axis, complete the coordination polyhedron to tetragonal bipyramid and bridge the copper atoms, forming chains running along the [001] axis. The dependence of the d–d band maximum on the Cu–O(axial) contact (2.755 (1) Å) and bipyramid distortion angle (5.0°) is discussed. The EPR parameters are also consistent with a CuN_2O_4 chromophore. The infrared spectra are discussed in comparison with those of other structurally known copper(II)–*N*-tosylglycinate complexes.

Introduction

The coordination behavior of *N*-tosylglycine toward copper(II) ion in the solid state and in aqueous solution, as a function of pH, has been investigated in our previous papers.[2,3] These studies have unequivocally demonstrated the importance of the tosyl group (4-toluenesulfonyl)[2] on the nitrogen atom in activating the coordination sites on the amino acid. In fact, at pH <5 only the carboxyl group binds the metal ion, the peptide nitrogen being undeprotonated,[2,3] while at pH ≥5 the presence of the tosyl group enables the deprotonation of the

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NH group, making it an excellent nucleophile.[4] This is accompanied by the coordination of the nitrogen atom, allowing the formation of very stable five-membered chelate rings.[2]

In the first case, the amino acid behavior parallels that of *N*-acetyl and *N*-benzoyl derivatives. In addition, the simple complexes of these react easily with amines to form monomeric tetragonally distorted bipyramidal bis(amine) adducts.[5-7] In particular, the reaction with unidentate aromatic amines sometimes leads to the formation of hydrate ternary complexes.[5-8]

Previous structural investigations performed on two complexes of the last type, diaquabis(*N*-acetyl-DL-tryptophanato)bis(pyridine)copper(II)[5] and bis(*N*-acetyl-α-alaninato)bis(*N*-methylimidazole)copper(II) dihydrate,[7] have revealed that the water molecules may adopt different arrangements in the unit cell, being coordinated in the pyridine adduct[5] and uncoordinated in the *N*-methylimidazole one.[7]

To verify whether this behavior is also characteristic of *N*-tosylglycine, we have now synthesized and characterized two of its hydrated pyridine adducts and, for one of them, *catena*-(μ-aqua)bis(*N*-tosylglycinato)bis(4-methylpyridine)copper(II), the crystal structure has also been determined. Moreover, the knowledge of a further new structure of a copper(II)-*N*-tosylglycinate complex enabled us to complete an exhaustive picture of the physical properties of the (*N*-tosylglycinato)copper(II) complexes.

Experimental Section

All chemicals were of reagent grade and used as received.

Preparation of *catena*-(μ-Aqua)bis(*N*-tosylglycinato)bis(4-methylpyridine)copper(II) [Cu(TsglyH)$_2$(4-Mepy)$_2$·H$_2$O]. The complex was prepared by adding to a concentrated methanolic solution of [Cu(TsglyH)$_2$·4H$_2$O] complex[2] the amine in a 1:2 molar ratio. Diethyl ether was added until the solution became pale blue; when the mixture was allowed to stand overnight at 4–5 °C, light blue crystals separated. Anal. Calcd for $C_{30}H_{36}CuN_4O_9S_2$: C, 49.72; H, 5.01; N, 7.74; S, 8.86; H$_2$O, 2.49. Found: C, 50.16; H, 5.20; N, 7.74; S, 8.70; H$_2$O, 2.48.

Preparation of [Cu(TsglyH)$_2$(py)$_2$·H$_2$O]. The amine was added to a warm concentrated enthanolic solution of [Cu(TsglyH)$_2$·4H$_2$O][2] in a 1:2 molar ratio. A pale blue microcrystalline compound instantaneously separated. Anal. Calcd for $C_{28}H_{32}CuN_4O_9S_2$: C, 48.28; H, 4.63; N, 8.05; S, 9.21; H$_2$O, 2.59. Found: C, 47.80; H, 4.80; N, 8.02; S, 9.06; H$_2$O, 2.60.

Physical Measurements. The electronic spectra of the solid compounds were recorded as mull transmission spectra with a Shimadzu MPS 50L spectrophotometer. The infrared spectra were recorded with a Perkin-Elmer 180 spectrophotometer as KBr pellets or as a Nujol mull on KBr as support in the 4000–250-cm^{-1} spectral range. The room-temperature magnetic moments were measured by the Gouy method using [Ni(en)$_3$S$_2$O$_3$] as calibrant and correcting for diamagnetism with the appropriate Pascal constants. The EPR spectra were recorded on a JEOL PE-3X spectrometer on polycrystalline samples with diphenylpicrylhydrazyl (DPPH, $g = 2.0036$) as a calibrating field marker. The thermogravimetric analysis was performed on a Mettler TA3000 instrument.

X-ray Crystallography: Data Collection, Structure Solution, and Refinement. A prismatic single crystal was selected for X-ray analysis and mounted approximately along its longest dimension. An automated Siemens AED diffractometer was used for determination of the cell dimensions and measurement of diffraction intensities. Cell dimensions, quoted in Table I, were determined by a least-squares treatment of 2ϑ values of 15 high-angle (ϑ above 22°) reflections accurately measured. Intensity data were collected by the ϑ–2ϑ scan technique within the angular range $3° < \vartheta < 27°$, and one reflection was measured every 50 reflections as a check on the alignment of the crystal and instrument stability. The individual reflection profile was analyzed as indicated from ref 9. The standard deviations were evaluated by a statistical counting, and 1965 unique reflections with $I > 2\sigma(I)$ were considered as observed and used in the analysis. Intensity data were corrrected for Lorentz and polarization effects but not for absorption because of the small size of the crystal and the low absorption coefficient (μ = 8.53 cm^{-1}).

Table I. Crystal Data

mol formula	$C_{30}H_{36}CuN_4O_9S_2$
mol wt	724.3
a, Å	19.089 (10)
b, Å	15.891 (5)
c, Å	10.883 (3)
β, deg	100.45 (1)
V, Å^3	3246 (2)
Z	4
d(obsd), g cm^{-3}	1.47
d(calcd), g cm^{-3}	1.48
space group[a]	*C*2/*c*
cryst dimens, mm	0.19 × 0.42 × 0.58
radiation (λ, Å)	Mo Kα (0.710 69) Nb filtered
2θ limits, deg	6–54
temp, °C	20 ± 1
abs coeff, cm^{-1} [b]	8.53
F(000)	1508
reflcns collcd	4994
unique data used ($I > 2\sigma(I)$)	1959
no. of variables	310
R	0.047
R_w	0.048

[a] From systematic absences and structural analysis. [b] $\mu\bar{r} = 0.13$; $A^* = 1.25$ over the range $\vartheta = 3–27°$'

Table II. Final Fractional Atomic Coordinates (×10^4) with Esd's in Parentheses

	x	*y*	*z*
Cu	0	0	0
S	2845 (1)	1024 (1)	2537 (1)
O(1)	1024 (2)	72 (3)	428 (4)
O(2)	1272 (2)	384 (3)	−1428 (5)
O(3)	3026 (3)	578 (3)	3671 (4)
O(4)	3390 (2)	1268 (3)	1882 (5)
O(5)	0	271 (5)	2500
N(1)	2305 (3)	440 (3)	1620 (5)
N(2)	−50 (2)	1237 (3)	−189 (4)
C(1)	1417 (3)	341 (4)	−292 (6)
C(2)	2123 (3)	676 (5)	315 (6)
C(3)	2387 (3)	1932 (4)	2815 (5)
C(4)	1897 (4)	1885 (5)	3579 (8)
C(5)	1521 (5)	2590 (5)	3755 (8)
C(6)	1604 (3)	3331 (4)	3187 (6)
C(7)	2111 (4)	3359 (5)	2449 (7)
C(8)	2495 (3)	2674 (4)	2246 (7)
C(9)	1152 (4)	4086 (5)	3348 (7)
C(10)	−464 (3)	1620 (4)	−1131 (5)
C(11)	−450 (3)	2464 (4)	−1328 (6)
C(12)	5 (3)	2971 (4)	−535 (6)
C(13)	421 (4)	2575 (4)	453 (7)
C(14)	383 (4)	1733 (4)	605 (7)
C(15)	49 (4)	3896 (4)	−737 (8)

The structure was solved by Patterson and Fourier methods and refined by least squares, first isotropically and then anisotropically, to the conventional *R* index of 6.8%. At this stage, the ΔF map revealed all hydrogen atoms, which are included in the refinement with isotropic thermal parameters. The final *R* index was 0.047, and $R_w = 0.048$. The function minimized was $\sum w|\Delta F|^2$; discrepancy indices used below are $R = \sum|\Delta F|/\sum F_o$ and $R_w = [\sum w|\Delta F|^2/\sum wF_o^2]^{1/2}$, the weighting scheme being $w = k/[\sigma^2(F_o) + g(F_o)^2]$, where $k = 0.9341$ and $g = 0.001\,415$. The atomic scattering factors used,

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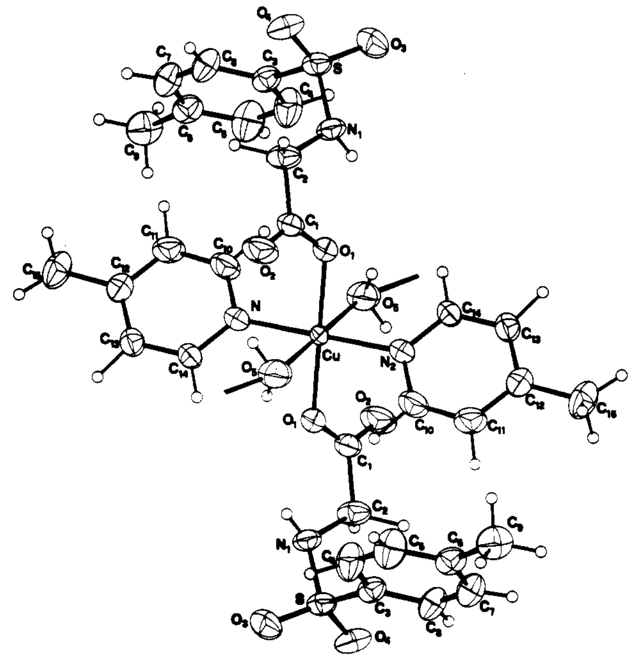

Figure 1. ORTEP view of the $[Cu(TsglyH)_2(4\text{-}Mepy)_2 \cdot H_2O]$ complex showing the atom numbering and the thermal motion ellipsoids (40%) for non-hydrogen atoms. The hydrogen atoms are represented as spheres of arbitrary radii.

corrected for anomalous dispersion, were taken from ref 10. Six reflections (−2,0,2; −6,0,2; 2,0,2; −1,1,2; 0,2,2; −3,1,4) were excluded from the final refinement as affected by counting error. The positional parameters for Cu, S, O, N, and C are given in Table II, but those for hydrogen atoms are available in the supplementary material. All the calculations were performed by using the CYBER 76 of the Centro di Calcolo Interuniversitario dell'Italia, Nord Orientale, Bologna, with the SHELX system of programs.[11]

Analysis. Nitrogen, carbon, hydrogen, and sulfur were analyzed with a C. Erba Model 1106 elemental analyzer instrument by G. Pistoni. The water was determined thermogravimetrically.

Results and Discussion

Description of the Structure. Figure 1 presents the molecular structure of the title compound, and the bond distances and angles are quoted in Table III.

Environment of the Copper Atom. The most relevant feature of this structure is the copper atom coordination. Two centrosymmetrically disposed amino acids and 4-methylpyridine molecules coordinate with the copper in a square-planar arrangement (Cu–O(1) = 1.929 (4) Å, Cu–N(2) = 1.977 (5) Å, O(1)···N(2) = 2.753 (6) Å, O(1)···N(2)^i = 2.771 (6) Å (i = $\bar{x}$, $\bar{y}$, $\bar{z}$)). The elongated tetragonal bipyramid around the copper atom is completed by water molecules (Cu···O(5) = 2.755 (1) Å) lying on the twofold axis and bridging the copper atom to form a polymeric chain running along the [001] axis with the Cu–O(5)–Cu angle at 162.0 (3)°. This kind of polymeric structure, whose site symmetry about the copper(II) ions is depicted for clarity in Figure 2, so far never found for copper(II)-*N*-protected amino acid complexes, was also observed in bis(acetato)bis(*p*-toluidine)copper(II) trihydrate ($[Cu(CH_3COO)_2(p\text{-tol})_2 \cdot H_2O] \cdot 2H_2O$)[12a] and in *catena*-tris(μ-aqua)bis(*N*-benzoylglycinato)metal(II) dihydrate ($[M(Hippu)_2 \cdot 3H_2O]2H_2O$; M(II) = Fe(II),[12b] Co(II), Ni(II)[12c]). In particular, in the copper(II) complexes there is a relationship between the M–O(axial) distances and the M–O–M′ angles (2.755 (1) Å and 162.0 (3)° in this work and 2.595 (3) Å and 131.1 (3)° in ref 12a).

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

Cu–O(1)	1.929 (4)	Cu–O(5)	2.755 (1)
Cu–N(2)	1.977 (5)		
C(1)–O(1)	1.254 (8)	C(6)–C(7)	1.366 (11)
C(1)–O(2)	1.219 (8)	C(7)–C(8)	1.353 (10)
C(1)–C(2)	1.488 (8)	C(6)–C(9)	1.506 (10)
N(1)–C(2)	1.449 (8)	N(2)–C(10)	1.324 (7)
N(1)–S(1)	1.596 (5)	C(10)–C(11)	1.359 (9)
S(1)–O(3)	1.411 (4)	C(11)–C(12)	1.370 (8)
S(1)–O(4)	1.418 (5)	C(12)–C(13)	1.369 (9)
S(1)–C(3)	1.742 (6)	C(13)–C(14)	1.352 (9)
C(3)–C(4)	1.362 (11)	N(2)–C(14)	1.339 (8)
C(4)–C(5)	1.363 (12)	C(12)–C(15)	1.491 (9)
C(5)–C(6)	1.353 (10)		
O(1)–Cu–N(2)	89.6 (2)	O(1)–Cu–O(5)	86.2 (2)
N(2)–Cu–O(5)	86.5 (2)		
O(1)–C(1)–O(2)	127.0 (6)	C(4)–C(5)–C(6)	122.9 (8)
O(1)–C(1)–C(2)	116.2 (5)	C(5)–C(6)–C(7)	116.8 (7)
O(2)–C(1)–C(2)	116.8 (6)	C(6)–C(7)–C(8)	122.2 (7)
C(1)–C(2)–N(1)	112.3 (5)	C(3)–C(8)–C(7)	119.3 (6)
C(2)–N(1)–S(1)	118.4 (4)	C(5)–C(6)–C(9)	121.5 (6)
N(1)–S(1)–O(3)	106.4 (3)	C(7)–C(6)–C(9)	121.6 (6)
N(1)–S(1)–O(4)	107.1 (3)	C(10)–N(2)–C(14)	116.2 (5)
N(1)–S(1)–C(3)	107.6 (3)	N(2)–C(10)–C(11)	123.3 (5)
O(3)–S(1)–O(4)	119.4 (5)	C(10)–C(11)–C(12)	120.6 (6)
O(3)–S(1)–C(3)	108.4 (3)	C(11)–C(12)–C(13)	115.8 (6)
O(4)–S(1)–C(3)	107.3 (3)	C(12)–C(13)–C(14)	121.0 (7)
C(4)–C(3)–C(8)	120.1 (6)	C(13)–C(14)–N(2)	123.0 (7)
S(1)–C(3)–C(8)	121.0 (5)	C(11)–C(12)–C(15)	122.2 (6)
S(1)–C(3)–C(4)	118.9 (5)	C(13)–C(12)–C(15)	121.9 (6)
C(3)–C(4)–C(5)	118.6 (7)		

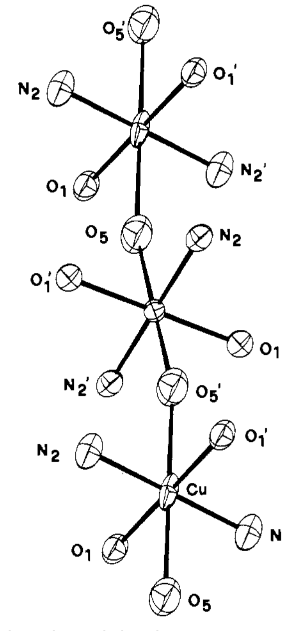

Figure 2. Projection view of the site symmetry about the Cu(II) ions.

The equatorial atoms of our compound are strictly coplanar as required by symmetry, the distortion of the bipyramid being measured by the angle between the Cu–O(5) vector and the normal to the equatorial plane (5.0)°. In Table IV the Cu···O(axial) distances and bipyramidal distortion angles of some compounds are reported. In complexes **1–3**, in which the axial positions are occupied by oxygen atoms of water molecules, which do not undergo any constraint, this angle is close to 0°. For complexes **4–6**, the angle markedly increases

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Table IV. Correlation between (Cu···O) Axial Distances (Å), Bipyramid Distortion Angles (deg), and d–d Band Maxima ($cm^{-1} \times 10^3$) for Some Complexes Having Distorted Octahedral Coordination[a]

no.	complex	$(Cu\cdots O)_{axial}$ dist	distortion angle	d–d band max	ref
1	$[Cu(CH_3COO)_2(p\text{-tol})_2 \cdot H_2O] \cdot 2H_2O^b$	2.595 (3)	9.6		12a
2	$[Cu(Actrp)_2(py)_2(H_2O)_2]^b$	2.61 (1)	2.7	15.9	5
3	$[Cu(TsglyH)_2(4\text{-Mepy})_2 \cdot H_2O]^b$	2.755 (1)	5.0	15.9	this work
4	$[Cu(Ac\text{-}\alpha\text{-ala})_2(N\text{-MeIm})_2] \cdot 2H_2O^c$	2.907 (4)	41.1	18.2	7
5	$[Cu(Hippu)_2(Im)_2]^c$	2.736 (4)	37.2	17.5	6
6	$[Cu(TsglyH)_2(N\text{-MeIm})_2]^c$	2.758 (4)	37.8	17.9	3

[a] Abbreviations: Actrp = *N*-acetyltryptophanate ion; Ac-α-ala = *N*-acetyl-DL-alaninate ion; Im = imidazole; *N*-MeIm = *N*-methylimidazole. For other abbreviations, see text. [b] Oxygen atom of a water molecule. [c] Oxygen atom of a carboxylic group.

Table V. More Relevant IR Bands (cm^{-1}) of *N*-Tosylglycinate–Copper(II) Complexes

no.	complex	$\nu(NH)$	$\nu(OCO)_{as}$	$\nu(OCO)_s$	$\nu(SO_2)_{as}$	$\nu(SO_2)_s$	$\nu(SN)$	ref
7	$[Cu(Tsgly)(H_2O)_3]$		1615 vs	1395 vs	1245 vs	1132 vs, 1113 vs	978 s	2
8	$K_2[Cu(Tsgly)_2]$		1605 vs	1390 vs	1268 vs	1140 vs, 1105 vs	982 vs 954 s 938 s 927 ms	2
9	$[Cu(TsglyH)_2(N\text{-MeIm})_2]$	3200 s	1620 vs	1380 vs	1330 vs	1165 vs	900 s	3
10	$[Cu(TsglyH)_2(4\text{-Mepy})_2 \cdot H_2O]^a$	3280 s	1595 vs	1382 vs	1325 vs	1160 vs	905 s	this work
11	$[Cu(TsglyH)_2(py)_2 \cdot H_2O]^a$	3250 s	1605 vs	1395 vs	1325 vs	1165 vs, 1155 vs	870 s	this work

[a] $\nu(OH)_{water}$ = 3400 sh.

as the axial positions are occupied by the second carboxylate oxygens. This fact, directly connected with d–d energy bands, will be discussed elsewhere.

It is also interesting to compare the coordination of *N*-tosylglycine in the present complex with those of other copper(II) complexes previously examined. In $[Cu(Tsgly)(H_2O)_3]$[2] and in $K_2[Cu(Tsgly)_2]$,[2] the *N*-tosylglycine molecules participate in the copper coordination through one carboxylate oxygen and the deprotonated sulfonamide nitrogen, forming stable five-membered chelate rings while, in $[Cu(TsglyH)_2(N\text{-MeIm})_2]$[3] and in the present complexes, the sulfonamide nitrogen is undeprotonated and uncoordinated and only the carboxylate group coordinates the copper. The different behaviors were demonstrated to be strictly dependent on the basicity of the media.[2,3] Furthermore, in the 4-methylpyridine adduct, where the carboxylate group is truly monodentate toward the copper atom, the Cu–O(1) distance (1.929 (4) Å) becomes comparable with those found in other copper(II) complexes with monodentrate carboxylate groups[13,14] and in $[Cu(Tsgly)(H_2O)_3]$ (Cu–O = 1.931 (4) Å) and $K_2[Cu(Tsgly)_2]$ (Cu–O(1) = 1.923 (4), 1.954 (4) Å).

***N*-Tosylglycinate Ligand.** Bond distances and angles in the amino acid agree well with those found in previously cited Cu complexes, the S–N bond (1.596 (5) Å) being comparable with those found in uncoordinated sulfonamides (1.606–1.650 Å).[15-18] As shown by the analysis of the planarity quoted in supplementary material, the C^{α}–COO group is planar with the amide nitrogen, displaced 0.296 Å out of the mean plane (0.298 Å in $[Cu(TsglyH)_2(N\text{-MeIm})_2]$), and forms angles of 87.4 and 61.3° with the mean plane through the benzene and picoline rings, respectively. The latter two planes are mutually orthogonal, the dihedral angle being 89.9°. The conformation of the glycinate moiety is described by using torsion angles around C–C and C–N bonds, 14.6 (8) and −154.7 (4)°, respectively. In $[Cu(Tsgly)(H_2O)_3]$, the corresponding angles are 10.3 (7), −173.6 (4) and 1.2 (9), 1.7 (9), 177.5 (5), 151.4 (5)°, respectively. In $[Cu(TsglyH)_2(N\text{-MeIm})_2]$, the contact involving the second carboxylic oxygen in the coordination makes the torsion angle values −167.3 (4) and 172.9 (4)°.

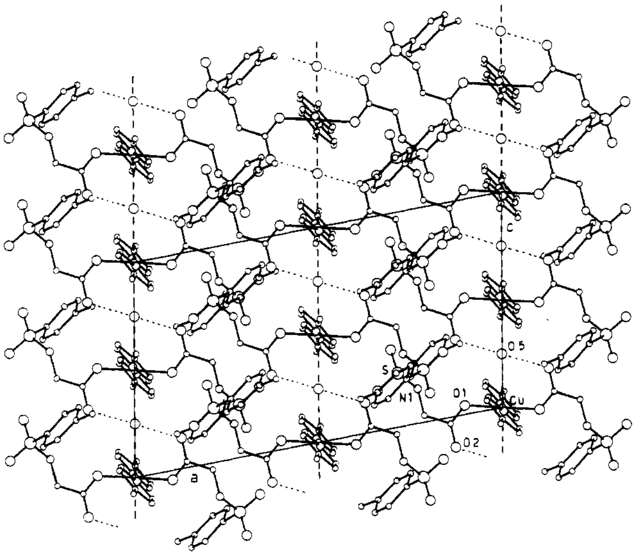

Figure 3. Projection along the *b* axis.

Hydrogen Bonding (Figure 3). The water molecule appears to be involved in two short hydrogen bonds with two uncoordinated carboxylic oxygens related by the twofold axis ($O(5)\text{–}H\cdots O(2)^{ii}$ = 2.704 (5) Å, O(5)–H = 0.90 (5) Å, $H\cdots O(2)^{ii}$ = 1.82 (5) Å, $O(5)\text{–}H\cdots O(2)^{ii}$ = 165.0 (3)° (ii = $x, \bar{y}, 1/2 + z$)). A long contact between the amide nitrogen and the carboxylic oxygen ($N(1)\text{–}H\cdots O(2)^{ii}$ = 3.441 (8) Å, N(1)–H = 0.85 (6) Å, $H\cdots O(2)^{ii}$ = 2.61 (6) Å, $N(1)\text{–}H\cdots O(2)^{ii}$ = 157.0 (3)°) and van der Waals contacts complete the packing in all directions.

Spectroscopic Results. The room-temperature magnetic moment (μ_{eff} = 1.78 μ_B) of the title complex falls into the range of monomeric magnetically dilute copper complexes. A possible superexchange coupling must occur via the apical water molecule, whose Cu···O bond is (a) long and (b) orthogonal to the unpaired electron in an effectively $d_{x^2-y^2}$ orbital. Consequently, it is expected to be very small.[19]

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The three EPR *g* values ($g_3 = 2.234$, $g_2 = 2.074$, $g_1 = 2.050$), in agreement with the geometry of the complex, are very similar to those reported for other elongated octahedral complexes[5,12a,20] with the CuN_2O_4 chromophore.

The room-temperature electronic spectrum of our compound, which shows a broad maximum centered at 15.9×10^3 cm^{-1} (Table IV), also indicates an elongated octahedral ligand field with a CuN_2O_4 chromophore.

In Table IV the Cu···O axial distances, the distortion angles, and the electronic spectra for a series of similar complexes are compared. It is observed that for complexes **2**, **3**, **5**, and **6**, which show axial and equatorial copper–ligand bond lengths comparable, there is a dependence of the electronic spectra on the distortion angles. In fact this angle is a measure of the metal–ligand orbital overlap, which increases as the angle decreases.[21] Therefore, for complexes **1**, **2**, and **3**, the Cu–O axial contact must be considered a true bond interaction, and their d–d band maximum is consistent with an elongated tetragonal-octahedral stereochemistry.[5] For complexes **5** and **6**, the value of the angle indicates an effective square-planar geometry as suggested from the d–d spectra.[21] All this reinforces the utility of electronic absorption spectroscopy in elucidating the probable coordination geometry of a metal ion.

The more relevant bands of the IR spectrum of the present complex are reported in Table V and compared with those of the other structurally known copper(II)–*N*-tosylglycinate complexes.[2,3] The main differences between deprotonated (complexes **7** and **8**) and undeprotonated (complexes **9** and **10**) in *N*-tosylglycinate derivatives are observed in the NH, SO_2, and SN stretching frequency regions. In fact, $\nu(SO_2)$ and $\nu(SN)$ at lower and higher energies, respectively, in complexes **7** and **8** than in complexes **9** and **10** is a consequence of the lengthening of the S–O bond and the shortening of the S–N bond due to the sulfonamide nitrogen deprotonation ($\nu(NH)$ is absent in deprotonated complexes). In complexes **9** and **10** $\nu(NH)$ appears at greater energy in the 4-methylpyridine adduct than in the *N*-methylimidazole adduct as, in the first complex, the NH group is involved only in one hydrogen-bonding interaction. It is also worthy of note that for all the complexes reported in Table V there are no appreciable differences in band shapes and positions of the carboxylate stretching frequencies even though they are differently involved in the copper coordination. The presence of hydrogen bonding in which these groups are also involved makes this technique insufficient for assigning the coordination type of the carboxylate group.

As regards the pyridine adduct, we did not obtain suitable crystals for X-ray analysis but the strict similarity of the physical properties ($\mu_{eff} = 1.83\ \mu_B$; $g_\parallel = 2.242$, $g_\perp = 2.076$) and, in particular, of the d–d band shape and position (15.6×10^3 cm^{-1}), with those of the 4-Mepy adduct enables us tentatively to suggest the presence of an octahedral copper(II) environment also in this complex.

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Registry No. $[Cu(TsglyH)_2(4\text{-}Mepy)_2\cdot H_2O]$, 86365-39-1; $[Cu(TsglyH)_2(py)_2\cdot H_2O]$, 86365-41-5; $[Cu(TsglyH)_2\cdot 4H_2O]$, 86391-46-0.

Supplementary Material Available: Listings of van der Waals contacts, thermal parameters and bond distances for hydrogen atoms, anisotropic thermal parameters, selected least-squares planes, and final structure factors (17 pages). Ordering information is given on any current masthead page.

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Synthesis, Crystal Structure, and Molecular Geometry of $[(\eta^5\text{-}C_5H_5)_2Fe]_4[Bi_4Br_{16}]$, the Ferrocenium Salt of a "Cluster of Octahedra" Hexadecabromotetrabismuthate Counterion

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Ferrocene in the presence of sunlight, $BiBr_3$, and molecular oxygen is oxidized to the ferrocenium cation and precipitates as the crystalline product $[(\eta^5\text{-}C_5H_5)_2Fe]_4[Bi_4Br_{16}]$ along with a stoichiometric quantity of BiOBr. The ferrocenium salt crystallizes in the monoclinic space group $P2_1/c$ with $a = 14.294$ (4) Å, $b = 19.337$ (3) Å, $c = 12.269$ (2) Å, $\beta = 109.23$ (2)°, $V = 3202.1$ (13) Å^3, and $Z = 2$. The asymmetric unit consists of one-half anion and two independent cations. The structure was refined to discrepancy indices of $R_F = 5.5\%$ and $R_{wF} = 5.5\%$ for those 3202 reflections with $I > 3\sigma(I)$. The $(\eta^5\text{-}C_5H_5)_2Fe^+$ cations are unusual in that the inter-ring alignments are neither symmetrically staggered nor eclipsed; rather the angles of displacement are 7.3 and 23.4° from an eclipsed configuration. The $Bi_4Br_{16}^{4-}$ anion is the first example of a cluster of four edge-sharing distorted $BiBr_6$ octahedra. The terminal Bi–Br bond distances average 2.683 Å while the bridging Bi–Br bond distances average 3.025 Å. The structure is compared to other crystallographically characterized polybromobismuthate anions. A review of these data reveals a trans effect in bond distances as previously predicted from a force constant analysis of vibrational data.

Introduction

We previously reported the synthesis and crystallographically determined structures of the ferrocenium ion $(\eta^5\text{-}C_5H_5)_2Fe^+$ salts formed by the photochemically promoted oxidation of ferrocene by molecular oxygen in the presence of the group 5 trichlorides $AsCl_3$,[3] $SbCl_3$,[4] and $BiCl_3$.[5] In each

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