Table VIII

	X		
M	Cl	Br	I
Zn	A	A	A
Cd	B	B	A
Hg	B	B	A

is worth noting that for all class B compounds we found only one broad band for the metal–bridging halogen stretching vibrations instead of three, since probably the three expected frequencies have accidentally very similar values.

In the far-IR spectra of all our complexes, on the basis of their idealized symmetries two IR- and Raman-active M–N stretching vibrations are expected. In assigning these bands, which must occur in the same spectral range as those found in ethylenediamine and 1,3-propanediamine complexes (300–500 cm^{-1}),[16,17,19,20,22,36,37] one must proceed cautiously, as other vibrations may appear in the same positions. The differences in both infrared and Raman spectra of class A and B compounds could derive either from their structural differences or from different mixing of the M–N vibration with other vibrations. The latter assumption seems to be confirmed by an unusually large difference found between the asymmetric and symmetric M–N stretching frequencies. The bands reported in Table VII for the probable (M–N) stretching frequencies are assigned by comparing the spectra of the complexes with those of a series of $[MX_4(dmpdH_2)]$ complexes,[38] in which M–N bands are absent. Furthermore, the assignment of these bands also takes into account that differences in metal or halogen masses influence the M–N band position.

Conclusion

According to infrared, Raman, and X-ray analysis we classified the complexes of the group 2B metals of general formula $[M(dmpd)X_2]$ into two classes. Results are reported in Table VIII. Class A contains tetrahedral complexes and class B octahedral. In both classes the dmpd forms a six-membered chelate ring, which shows a "chair" conformation more (group B) or less (group A) flattened. Indeed the ratio between the metal and the halogen radii decides the complex geometry. When the halogen size is increased and/or the metal size is decreased, the tetrahedral coordination is preferred because of the difficulty of accommodating four rather than two large halogen atoms around a small metal center.

Acknowledgment. The authors are grateful to the Italian Consiglio Nazionale delle Ricerche (CNR) for financial support and the Centro Strumenti of the University of Modena for recording the IR spectra.

Registry No. I, 85336-89-6; II, 85336-90-9; III, 85354-82-1; $Zn(dmpd)I_2$, 85336-91-0; $Cd(dmpd)Cl_2$, 85336-99-8; $Cd(dmpd)I_2$, 85336-92-1; $Hg(dmpd)Cl_2$, 85337-01-5; $Hg(dmpd)Br_2$, 85337-03-7; $Hg(dmpd)I_2$, 85336-93-2; $[ZnCl_4][dmpdH_2]$, 85336-94-3; $[ZnBr_4][dmpdH_2]$, 85336-95-4; $[CdBr_4][dmpdH_2]$, 85336-96-5; $[HgI_4][dmpdH_2]$, 85336-97-6.

Supplementary Material Available: Tables of positional and thermal parameters, computed and observed structure factor moduli, nonbonding contacts involving halogen atoms, and IR and Raman stretching frequencies and two figures of IR and Raman spectra of $[MX_4]^{2-}$ complexes (24 pages). Ordering information is given on any current masthead page.

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Contribution from the Ministero della Pubblica Istruzione of Italy, Istituto di Chimica Generale ed Inorganica, University of Modena, 41100 Modena, Italy, Istituto di Chimica Generale, Centro di Studio per la Strutturistica Diffrattometrica del CNR, University of Parma, 43100 Parma, Italy, and Istituto di Chimica, Facoltà di Medicina-Veterinaria, University of Bari, 70126 Bari, Italy

Role of the Tosyl Group in the Coordination Ability of N-Protected Amino Acids. 3. Ternary Complexes of Copper(II) with *N*-Tosylglycine and Aromatic Amines. Crystal and Molecular Structure of Bis(*N*-tosylglycinato)bis(*N*-methylimidazole)copper(II)

L. P. BATTAGLIA,[1a] A. BONAMARTINI CORRADI,[1a] G. MARCOTRIGIANO,[1b] L. MENABUE,[1c] and G. C. PELLACANI*[1c]

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Some compounds of the type $Cu(TsglyH)_2X_2$ (TsglyH = *N*-tosylglycinate anion; X = imidazole, *N*-methylimidazole, and pyridine) have been prepared and characterized by means of magnetic moments and ESR, electronic, and infrared spectra. For one of them, bis(*N*-tosylglycinato)bis(*N*-methylimidazole)copper(II), the crystal structure has also been determined. The crystals are monoclinic ($P2_1/n$) with cell dimensions $a = 13.733$ (3) Å, $b = 8.766$ (2) Å, $c = 13.641$ (3) Å, $\beta = 105.97$ (5)°, and $Z = 2$. The structure has been determined from diffractometric data by Patterson and Fourier methods and refined by full-matrix least squares to an R value of 0.052. The complex has square-planar coordination via two centrosymmetric carboxylic oxygens and two imidazole nitrogens. Two weak interactions (2.758 Å) with two carboxylic oxygens complete the coordination to a strongly distorted tetragonal bipyramid. Packing is determined by N–H(amide)···O(carboxylate) hydrogen bonds and by van der Waals contacts. Electronic, infrared, and ESR spectra are consistent with this type of structure for all the complexes.

Introduction

In our previous investigation on the copper(II) ion–*N*-tosylglycinate system in the solid state and in aqueous solution,[2] it was suggested that the ligand presents the properties of both the L-α-amino acids[3] and their *N*-acetyl or *N*-benzoyl deriv-

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(1) (a) University of Parma. (b) University of Bari. (c) University of Modena.

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atives,[4,5] depending on the pH of the media. In fact at pH greater than 5, some compounds were separated in which the ligand was found to act as a bidentate ligand through an oxygen atom of the carboxylate group and a deprotonated nitrogen atom of the sulfonamide group, as the X-ray crystal structures performed on two of them have demonstrated.

For one complex, $Cu(TsglyH)_2 \cdot 4H_2O$ (TsglyH = *N*-tosylglycinate monoanion), separated at a pH lower than 5, the suggestion of a coordinative behavior of the amino acids through the carboxylate group, as previously found in the *N*-acetyl or *N*-benzoyl derivatives of the L-α-amino acids, was based only upon its spectroscopic and magnetic properties. As crystals suitable for X-ray analysis of this compound were not obtained, we have now investigated some of its ternary complexes by means of spectroscopic and magnetic measurements in order to determine carefully the ligand coordination sites. For one of the complexes, bis(*N*-tosylglycinato)bis(*N*-methylimidazole)copper(II), the crystal structure has also been determined.

Further interest in this work derives from its biological implications, since we are dealing with complexes containing imidazole and carboxylate groups, which are the ligating moieties found in proteins and in many naturally occurring mixed-ligand complexes.[6,7]

Experimental Section

Preparation of Bis(*N*-tosylglycinato)bis(imidazole)copper(II) and Bis(*N*-tosylglycinato)bis(*N*-methylimidazole)copper(II), $Cu(TsglyH)_2(Im)_2$ and $Cu(TsglyH)_2(N\text{-MeIm})_2$. Both complexes were prepared by mixing the $Cu(TsglyH)_2 \cdot 4H_2O$ complex[2] and the amine in a 1:2 molar ratio, in methanol. After the solution was allowed to stand, blue-violet crystals separated. Anal. Calcd for $Cu(TsglyH)_2(Im)_2$, $C_{24}H_{28}CuN_6O_8S_2$: C, 43.91; H, 4.30; N, 12.81; S, 9.78. Found: C, 43.87; H, 4.37; N, 12.74; S, 9.55. Calcd for $Cu(TsglyH)_2(N\text{-MeIm})_2$, $C_{26}H_{32}CuN_6O_8S_2$: C, 45.62; H, 4.72; N, 12.29; S, 9.38. Found: C, 45.80; H, 4.77, N, 12.28; S, 9.46.

Preparation of Bis(*N*-tosylglycinato)bis(pyridine)copper(II), $Cu(TsglyH)_2(py)_2$. The compound is prepared as reported above in ethanol. Anal. Calcd for $C_{28}H_{30}CuN_4O_8S_2$: C, 49.56; H, 4.46; N, 8.26; S, 9.46. Found: C, 49.23; H, 4.39; N, 8.07; S, 9.00.

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 in a Nujol mull on KBr pellets as support in the 4000–250-cm^{-1} spectral range. The room-temperature magnetic moments were measured by the Gouy method with $Ni(en)_3S_2O_3$ as calibrant and correction for diamagnetism with the appropriate Pascal constants. The ESR spectra were recorded on a JEOL PE-3X spectrometer on polycrystalline samples with diphenylpicrylhydrazyl (DPPH, $g = 2.0036$) as calibrating field marker.

X-ray Data Collection and Structure Determination. The crystal and refinement 1106, are summarized in Table I. Cell dimensions were determined by diffractometry with an "on line" single-crystal Siemens AED diffractometer and refined by least squares with use of 2ϑ values of 15 accurately measured high-angle reflections ($110° \leq 2\vartheta \leq 140°$). The intensities were collected on the diffractometer with Ni-filtered Cu Kα radiation ($\bar{\lambda} = 1.5418$ Å). One reflection was measured after 50 reflections as a check on alignment and on crystal and instrument stability. The individual reflection profiles were analyzed as described by Grant and Gabe.[8] With an acceptance criterion of $I > 2\sigma(I)$, 2435 reflections were retained. Lorentz and polarization corrections were applied, but not absorption corrections, as the $\mu\bar{r}$ value was very low (0.26), and if a cylindrical shape is assumed for the crystal, the absorption correction coefficients are practically invariant over the ϑ range 4–70° ($A^* = 1.52$–1.50). The structure was solved by the heavy-atom technique and refined by the least-squares method with anisotropic temperature factors for all non-hydrogen atoms to $R = 0.081$. A successive ΔF map revealed the positions of hydrogen atoms, which are introduced in the refinement with isotropic thermal parameters. The final R ($R = \sum|\Delta F|/\sum|F_o|$) was 0.052, and R_w ($R_w = [(\sum w(|\Delta F|)^2/(\sum wF_o)^2]^{1/2}$) was 0.054. Five reflections ($\bar{1}01$, $\bar{3}11$, $\bar{2}11$, $\bar{1}21$, $\bar{2}12$) were excluded from the final refinement since they were affected by extinction or counting errors. The atomic scattering factors, corrected for anomalous dispersion, were taken from ref 9. The function minimized in the least-squares calculations $\sum w|\Delta F|^2$, with the weighting scheme $w^{-1} = \sigma^2(F_o) + 0.01732(F_o)^2$. All the calculations were performed with use of the CYBER 76 computer at the Centro di Calcolo dell'Italia Nord-Orientale, Bologna, Italy, with the SHELX[10] system of programs. Final atomic coordinates are listed in Table II.

Table I. Crystal Data for $[Cu(TsglyH)_2(N\text{-MeIm})_2]$

molecular formula	$C_{26}H_{32}CuN_6O_8S_2$
mol wt	684.24
a, Å	13.733 (3)
b, Å	8.766 (2)
c, Å	13.641 (3)
β, deg	105.97 (5)
V, Å^3	1578.8 (7)
Z	2
d_{obsd}(by flotation), g·cm^{-3}	1.42
d_{calcd}, g·cm^{-3}	1.44
space group	$P2_1/n$
cryst dimens, mm	0.11 × 0.29 × 0.52
radiation ($\bar{\lambda}$, Å)	Cu Kα, Ni filtered (1.54178)
2ϑ limits, deg	6–140
temp, °C	20
abs coeff, cm^{-1}	26.4
$F(000)$, electrons	710
unique data used ($I > 2\sigma(I)$)	2435
no. of variables	252
R	0.052
R_w	0.054

Analysis. Sulfur, nitrogen, carbon, and hydrogen were analyzed with a C. Erba elemental analyzer, Model 1106, by G. Pistoni.

Results and Discussion

Description of the Structure of Bis(*N*-tosylglycinato)bis(*N*-methylimidazole)copper(II). A drawing of the structure showing the atom numbering is given in Figure 1, and selected bond distances and angles are collected in Table III. The structure consists of copper atoms lying on the center of symmetry, square-planar coordinated via two centrosymmetric carboxylic oxygens and two imidazole nitrogen atoms (Cu–O(1) = 1.967 (4) Å, Cu–N(2) = 1.970 (4) Å; N(2)···O(1) = 2.974 (5) Å; O(1)···N(2)^i = 2.774 (5) Å (i = $\bar{x}$, $\bar{y}$, $\bar{z}$)). Two weak interactions (2.758 (4) Å) with two carboxylic oxygen atoms in the "out of plane" positions complete the very distorted tetragonal bipyramidal coordination. The equatorial atoms are strictly coplanar, as required by the symmetry, and the distortion of the coordination polyhedron, measured by the angle between the Cu–O(2) vector and the normal to the equatorial plane, is 37.8°.

This kind of structural arrangement is typical for carboxylate complexes and for the ternary complexes of N-protected amino acids (where the protecting group is an acetyl or a benzoyl group), which act as carboxylate ligands.[11,12] In

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Table II. Fractional Atomic Coordinates (×10^4) for the Cu(TsglyH)$_2$(*N*-MeIm)$_2$ Complex

atom	*x*/*a*	*y*/*b*	*z*/*c*	atom	*x*/*a*	*y*/*b*	*z*/*c*
Cu	0 (0)	0 (0)	0 (0)	C(11)	2695 (6)	269 (16)	2769 (7)
S	2232 (1)	6435 (2)	−745 (1)	C(12)	1907 (5)	−349 (9)	2922 (5)
O(1)	884 (2)	1252 (4)	−592 (2)	C(13)	971 (5)	−424 (8)	2253 (4)
O(2)	282 (3)	3115 (4)	162 (3)	H(1)	2056 (53)	3319 (75)	−779 (48)
O(3)	3214 (3)	5722 (6)	−552 (4)	H(2)	1156 (48)	3623 (69)	−1478 (49)
O(4)	2131 (4)	7852 (5)	−269 (4)	H(3)	975 (41)	5710 (68)	−401 (40)
N(1)	1488 (3)	5234 (5)	−405 (3)	H(4)	2716 (49)	5087 (61)	−2429 (47)
N(2)	1073 (3)	−130 (5)	1297 (3)	H(5)	2059 (46)	5312 (68)	−4213 (45)
N(3)	2592 (4)	−20 (7)	2380 (4)	H(6)	1092 (42)	7305 (65)	−5633 (42)
C(1)	805 (3)	2647 (5)	−373 (3)	H(7)	67 (59)	6084 (82)	−5626 (57)
C(2)	1414 (5)	3715 (6)	−842 (5)	H(8)	−45 (49)	8066 (71)	−5461 (48)
C(3)	1742 (4)	6655 (6)	−2071 (4)	H(9)	−97 (43)	8536 (65)	−3745 (42)
C(4)	2167 (4)	5854 (7)	−2717 (5)	H(10)	580 (40)	8162 (65)	−2000 (41)
C(5)	1748 (5)	5986 (8)	−3749 (5)	H(11)	2376 (45)	404 (62)	780 (44)
C(6)	913 (5)	6924 (8)	−4155 (5)	H(12)	4071 (47)	89 (62)	2257 (46)
C(7)	467 (8)	7066 (15)	−5290 (6)	H(13)	3882 (45)	1284 (72)	3098 (45)
C(8)	498 (6)	7700 (9)	−3484 (6)	H(14)	4017 (46)	−637 (73)	3335 (46)
C(9)	898 (5)	7574 (8)	−2459 (5)	H(15)	2083 (41)	−516 (67)	3731 (41)
C(10)	2052 (5)	121 (7)	1411 (4)	H(16)	265 (43)	−671 (67)	2435 (43)

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

(a) In the Coordination Polyhedron

Cu–O(1)	1.967 (3)	Cu–O(2)	2.758 (4)
Cu–N(2)	1.970 (4)		
O(1)–Cu–N(2)	90.4 (2)		

(b) In the Ligands

C(1)–O(1)	1.271 (6)	N(2)–C(10)	1.329 (8)
C(1)–O(2)	1.227 (6)	N(2)–C(13)	1.374 (7)
C(1)–C(2)	1.510 (8)	N(3)–C(10)	1.331 (7)
C(2)–N(1)	1.451 (7)	N(3)–C(11)	1.483 (10)
N(1)–S	1.621 (5)	N(3)–C(12)	1.378 (10)
S–O(3)	1.443 (4)	C(12)–C(13)	1.358 (8)
S–O(4)	1.426 (5)		
S–C(3)	1.758 (5)		
N(1)–S–C(3)	105.8 (3)	C(10)–N(2)–C(13)	106.5 (5)
O(4)–S–C(3)	108.4 (3)	C(10)–N(3)–C(11)	125.1 (6)
O(4)–S–N(1)	106.7 (3)	C(10)–N(3)–C(12)	106.0 (6)
O(3)–S–C(3)	108.0 (3)	C(11)–N(3)–C(12)	128.7 (6)
O(3)–S–N(1)	107.3 (3)	N(3)–C(10)–N(2)	111.7 (5)
O(3)–S–O(4)	119.8 (4)	N(3)–C(12)–C(13)	108.0 (6)
S–N(1)–C(2)	117.2 (4)	N(2)–C(13)–C(12)	107.7 (6)

Table IV. Contacts Less Than 3.5 Å[a]

O(1)···O(4)$^{\mathrm{i}}$	3.405 (6)	C(11)···O(2)$^{\mathrm{ii}}$	3.365 (11)
N(2)···O(4)$^{\mathrm{i}}$	3.393 (7)	O(2)···O(2)$^{\mathrm{iii}}$	3.395 (5)
C(10)···O(4)$^{\mathrm{i}}$	3.059 (8)	O(2)···O(4)$^{\mathrm{iii}}$	3.462 (7)

[a] Superscripts for the oxygen atoms indicate the following transformations: i = $x, y-1, z$; ii = $^1/_2 - x, y - {}^1/_2, {}^1/_2 - z$; iii = $\bar{x}, 1-y, \bar{z}$.

particular, in bis(hippurato)bis(imidazole)copper(II) the corresponding distances and angle (Cu–O = 1.976 (3) Å, Cu–N = 1.964 (3) Å, Cu···O(axial) = 2.736 (4) Å, and 37.2°)[11] are very close to those found in the present complex, while in bis(*N*-acetyl-α-alaninato)bis(*N*-methylimidazole)copper(II) hydrate the shortest equatorial coordination distances (Cu–O = 1.942 (3) Å, Cu–N = 1.959 (5) Å) are associated with the longest "out of plane" interaction (2.907 (4) Å).[12]

In the present complex, only the amide nitrogen is suitable for hydrogen bonds (Table IV). In fact, packing (Figure 2) is determined by an NH(amide)···O hydrogen bond (N(1)–H(3)···O(2)$^{\mathrm{i}}$ = 2.925 (6) Å (i = $\bar{x}, \bar{y}, \bar{z}$), N(1)–H(3) = 0.82 (6) Å, H(3)···O(2)$^{\mathrm{i}}$ = 2.11 (6) Å, N(1)–H(3)···O(2)$^{\mathrm{i}}$ = 171.8°), involving the weakly coordinated carboxylic oxygen atom, and by van der Waals contacts quoted in Table IV. The SO_2 group is only involved in this last type of interaction.

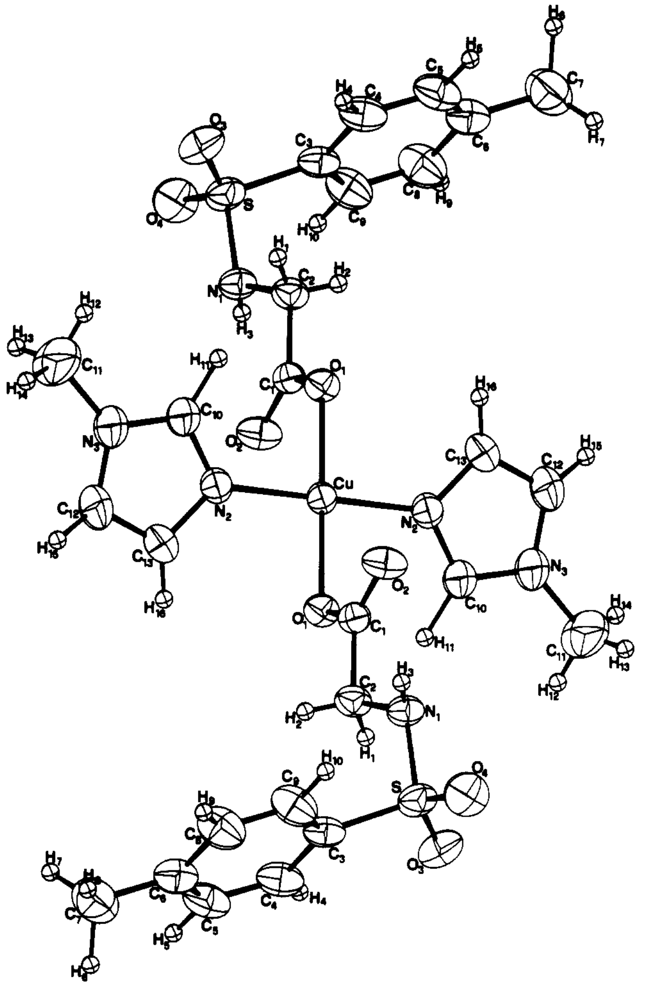

Figure 1. ORTEP view of the Cu(TsglyH)$_2$(*N*-MeIm)$_2$ complex showing the atom numbering and the thermal motion ellipsoids (40%) for the non-hydrogen atoms. The hydrogen atoms are represented as spheres of arbitrary radius.

A structural investigation performed on two (*N*-tosylglycinato)copper(II) complexes separated from aqueous solution at a pH greater than 5 had shown that the amino acid behaved as a bidentate ligand through deprotonated sulfonamide nitrogen and carboxylate oxygen atoms, forming stable five-membered chelate rings, which favor the five-coordination of the metal ion. The structural results on the Cu-

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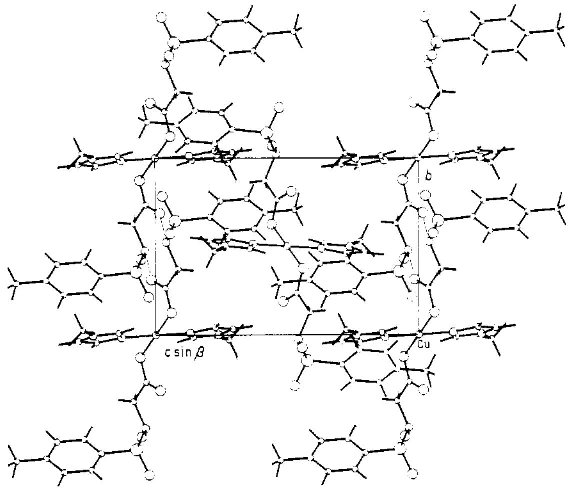

Figure 2. Projection along the *a* axis of the packing of the Cu-$(TsglyH)_2(N\text{-}MeIm)_2$ complex.

$(TsglyH)_2(N\text{-}MeIm)_2$ complex shows that *N*-tosylglycine may also act as a simple carboxylic acid when the basicity of the medium is unable to deprotonate the sulfonamide nitrogen atom. Coordinating as a simple carboxylate acid, the amino acid becomes a weak ligand for the copper(II) ion, so that, as the weak ligand field of the in-plane donors strengthens the axial interactions, a tetragonal coordination is favored. This evidence reinforces our conviction that in the parent Cu-$(TsglyH)_2 \cdot 4H_2O$ complex, also, the *N*-tosylglycine coordinates solely through the carboxylate group.[2]

The variable pH-dependent coordinative behavior of *N*-tosylglycine, greater than that observed in the *N*-acetyl or *N*-benzoyl derivatives of the amino acids, clearly depends on the presence of the tosyl group, which has a strong inductive electrophilic effect, so that the anion of the sulfonamide group becomes an excellent nucleophile.[13]

Bond distances and angles in the *N*-tosylglycinate monoanion found in bis(*N*-tosylglycinato)bis(*N*-methylimidazole)copper(II) are similar to those of other previously examined complexes,[2] the only difference being observed for the S–N(1) distance, which is longer in the former complex (1.621 (5) Å) than in the latter (1.570–1.580 Å), in agreement with the presence in the latter complexes of a coordinated deprotonated nitrogen atom. In the uncoordinated sulfonamides, also, the S–N distance is 1.606–1.650 Å.[14-17]

As shown by analyses of the planarity (supplementary material), the C^{α}–COO group is planar and practically orthogonal to the benzene ring (the dihedral angle being 106.1°). The sulfonamide nitrogen is displaced 0.298 Å out of the carboxylate plane. Moreover, the mean plane through the carboxylate group forms an angle of 44.5° with the sulfonamide moiety.

The conformation of the glycinate moiety can be described by using torsion angles around C–N and C–C bonds, C(1)–C(2)–N(1)–S = 172.9 (4)°, O(1)–C(1)–C(2)–N(1) = –167.3 (4)°, corresponding to the extended form for the amino acid.

Spectroscopic Results. Band shapes, and positions of the room-temperature electronic spectra of all the complexes (Table V) are very similar to one another and consistent with the presence of a strongly distorted tetragonally elongated ligand field.[18,19] A correlation between the d–d band maximum of the electronic spectrum and the Cu···O axial distance for several complexes is reported in Table VI.

Table V. Magnetic, Electronic, and Infrared Results for the Solid Complexes

	$Cu(TsglyH)_2$-$(N\text{-}MeIm)_2$	$Cu(TsglyH)_2$-$(py)_2$	$Cu(TsglyH)_2$-$(Im)_2$
μ_{eff}, μ_B	1.87	1.90	1.79
$g_{\parallel}$	2.249	2.204	2.175 (g_3)
$g_{\perp}$	2.053	2.028	2.102 (g_2)
10^4A, cm^{-1}	189	206	2.053 (g_1)
d–d bands, 10^{-3} cm^{-1}	15.4 sh 17.9	15.9 sh 18.2	15.4 sh 18.0
$\nu(NH)$,[a] cm^{-1}	3200 s	3240 s	3240 s
$\nu(OCO)_{asym}$, cm^{-1}	1620 vs	1620 vs	1625 vs
$\nu(OCO)_{sym}$, cm^{-1}	1380 vs	1375 vs	1365 vs
$\nu(SO_2)_{asym}$, cm^{-1}	1330 vs	1325 vs	1325 vs
$\nu(SO_2)_{sym}$, cm^{-1}	1165 vs	1165 vs	1165 vs
$\nu(SN)$, cm^{-1}	900 s	905 s	880 s

[a] NH stretching band of the amino acid. That of the imidazole, in $Cu(TsglyH)_2(Im)_2$, appears at 3320 s cm^{-1}.

Table VI. Correlation between d–d Band Maxima and Shortest Axial Interactions for Some Complexes Having an Elongated-Octahedral Configuration

	d–d band max, 10^{-3} cm^{-1}	$Cu\cdots O_{axial}$[a] dist, Å
$Cu(Ac\text{-}\alpha\text{-}ala)_2(N\text{-}MeIm)_2 \cdot H_2O$	18.2	2.907 (4)
$Cu(TsglyH)_2(N\text{-}MeIm)_2$	17.9	2.758 (4)
$Cu(Hippu)_2(Im)_2$	17.5	2.736 (4)

[a] Oxygen atom of the carboxylic group.

All the solid complexes show "normal" room-temperature magnetic moments and polycrystalline ESR spectra (Table V) of an axial type, suggesting an essentially $d_{x^2-y^2}$ ground state. The experimental *g* and *A* values are in the range expected for similarly distorted octahedral complexes.[20,21]

The IR spectra of the three compounds, very similar to one another in band shape and position (Table V), also closely resemble those found for the alkali salts of the ligand and that found for the $Cu(TsglyH)_2 \cdot 4H_2O$ complex,[2] confirming an amino acid coordination through the carboxylate group in this last complex, also. In particular, in our complexes the SO_2 (asymmetric and symmetric) and SN stretching band positions (1325–1330, 1165, and 880–905 cm^{-1}, respectively) are different with respect to those found in other previously examined copper(II)-*N*-tosylglycinate complexes (1245–1268, 1108–1140, and 958–978 cm^{-1}, respectively[2] and agree with the presence of a longer S–N(1) distance, the amide nitrogen atom being undeprotonated and uncoordinated.

The similarity of the spectroscopic properties enables us to suggest for all these bis(amine) adducts the presence of a CuN_2O_2 chromophore. In particular, these ternary systems containing heteroatomic amine–Cu^{2+}–O ligating moieties were found to be more stable than the corresponding binary complexes containing oxygen donor ligands, since the amines enhance the affinity of Cu(II) for oxygen donor sites of anionic ligands.[7] Therefore, these systems may be used as realistic

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mimics for copper enzymes or copper nonenzymatic proteins, especially for "blue proteins" of type 2 Cu.[22]

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Registry No. Cu(TsglyH)$_2$(Im)$_2$, 85479-91-0; Cu(TsglyH)$_2$(*N*-MeIm)$_2$, 85479-92-1; Cu(TsglyH)$_2$(py)$_2$, 85506-84-9; Cu(TsglyH)$_2\cdot$4H$_2$O, 85337-91-3.

Supplementary Material Available: Listings of selected least-squares planes, distances involving hydrogen atoms, bond distances and angles in tosylate benzene rings, and final structure factors (17 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Inorganic Chemistry,
The Royal Institute of Technology, Stockholm, Sweden

Crystal Structure of Tetraoxotetrahydroxohexabismuth(III) Perchlorate Heptahydrate, $Bi_6O_4(HO)_4(ClO_4)_6\cdot 7H_2O$: An X-ray and Neutron Diffraction Study

BENGT SUNDVALL

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The structure of the title compound was determined from single-crystal X-ray and neutron diffraction data, collected by diffractometric methods. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with $Z = 4$, $a = 11.084$ (3) Å, $b = 16.992$ (2) Å, and $c = 17.387$ (3) Å. The structure was derived on the basis of the intensities of 3183 X-ray and 2679 neutron reflections by using Patterson and Fourier methods. Refinement by full-matrix least-squares methods gave the conventional *R* values 0.067 (X-rays) and 0.087 (neutrons). The structure contains discrete hexanuclear complexes $Bi_6O_4(HO)_4^{6+}$, ClO_4^- ions, and crystal water molecules. The bismuth complex has a slightly distorted octahedral arrangement of the Bi atoms, with the O atoms located above the octahedral faces. Each type of oxygen (oxide and hydroxide) forms a distorted tetrahedron surrounding the Bi octahedron, giving close to T_d symmetry of the complex. The short Bi---Bi distances in the complex vary between 3.633 (8) and 3.764 (8) Å (average 3.675 Å), the short Bi---O^{2-} distances between 2.10 (1) and 2.20 (1) Å (average 2.15 Å), and the short Bi---OH$^-$ distances between 2.29 (1) and 2.48 (1) Å (average 2.40 Å). The coordination of oxygen to Bi within the complex is trigonal bipyramidal, with the hydroxide oxygens at the axial apices and the oxide oxygens at two of the equatorial apices, the third being occupied by the lone 6s^2 electron pair of Bi. Each Bi coordinates four other oxygen atoms outside the complex at longer Bi---O distances, giving a total coordination number of 8. The coordination polyhedra are irregular. Infrared and Raman spectra of the complex both in solid state and in solution are consistent with this structure. All but three of the hydrogen atoms participate in hydrogen bonds, most of which are weak. The perchlorate ions are close to tetrahedral with an average Cl---O distance of 1.44 Å, the individual distances having estimated standard deviations of 0.01 Å.

Introduction

Several independent methods have proved that the main species in moderately acidic solutions of bismuth(III) over a wide range of metal concentrations is a hexanuclear complex. Reviews of the work are given in ref 1 and 2.

From the results of emf measurements, the formula $Bi_6(HO)_{12}^{6+}$ was proposed,[3] with the reservation that the emf method cannot distinguish between this formula and others with different numbers of water molecules. The occurrence of a hexanuclear species was confirmed in an X-ray solution study,[4] where the metal atoms were found to have an octahedral arrangement and the bridging HO$^-$ groups were assumed to be located above the octahedral edges. The oxygen atoms could not, however, be located with precision. Raman measurements on solutions and crystals of the perchlorate, as well as infrared measurements on crystals,[5,6] were interpreted by the same formula and geometric arrangement.

In an X-ray structure study[7] of the basic bismuth nitrate $BiONO_3\cdot{}^1/_2H_2O$, an alternative structure was suggested. The structure was proposed to contain hexanuclear aggregates of bismuth atoms, forming trigonal prisms. The light atoms could not be located, and no refinement of the Bi positions was performed. A reinvestigation[8] of the structure of this salt showed the proposed structure to be in error. It contains complexes $Bi_6O_4(HO)_4^{6+}$, very similar to those found in the present work, and the formula should accordingly be written $Bi_6O_4(HO)_4(NO_3)_6\cdot H_2O$.

This was confirmed by a simultaneous, independent investigation[9] by Lazarini. Virtually the only difference is that Lazarini, in view of IR spectroscopy[10] and TGA results,[11] considered also the water molecule and a nitrate group to be coordinated to Bi, i.e. writing the formula of the complex $[Bi_6(H_2O)(NO_3)O_4(HO)_4]^{5+}$.

Lazarini also found the same arrangement of Bi and O in two other structures. The compound $Bi_6O_4(HO)_4(NO_3)_6\cdot 4H_2O$[12] contains isolated $Bi_6O_4(HO)_4^{6+}$ units while in $Bi_6O_5(HO)_3(NO_3)_5\cdot 3H_2O$[13] there is a closely related complex $Bi_6O_5(HO)_3^{5+}$. In the latter compound the hexanuclear groups are linked in pairs through two intermolecular Bi---O bonds.

The present study has been undertaken in order to obtain more extensive structural evidence for the composition and geometry of the hexanuclear bismuth hydrolysis complex. A preliminary X-ray investigation of the basic perchlorate salt using film methods has been published earlier,[14] in which it was shown that the Bi atoms form discrete hexanuclear complexes with octahedral geometry.

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