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Structural and spectroscopic properties of N-benzenesulphonylglycine complexes with copper (II)

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In this paper are reported structural and spectroscopic properties of (*N*-benzenesulphonylglycinato) triaquacopper (II) (complex I) and dipotassium bis (*N*-benzenesulphonylglycinato) cuprate (II) (complex II). The crystals of (I) are monoclinic, space group $P2_1/c$, $Z = 4$, with $a = 12.736(4)$, $b = 10.292(3)$, $c = 10.402(3)$ Å, $\beta = 109.41(2)°$ while those of complex (II) are orthorhombic, space group *Pbca*, with $a = 23.333(8)$, $b = 10.508(4)$, $c = 16.989(5)$ Å. In both complexes the aminoacid molecules act as bidentate *via* carboxylic oxygen and the amide nitrogen atom; in (I) three water molecules complete the coordination to tetragonal pyramidal, while in (II) coordination is square planar, tetrahedrally distorted involving two ligand molecules. The structure (I) was refined to a final R index of 0.0596 and (II) to $R = 0.0466$.

Introduction

N-ArSO$_2$-α-aminoacids form with Cu(II) ion solution bis-carboxylate complexes stable enough to undergo at pH > 5 sulphonamide nitrogen deprotonation with closure of a glycine like *N,O*-chelate ring (Antolini *et al.*, 1983). So the [Cu(LNO)] and $[Cu(LNO)_2]^{2-}$ species are successively formed, depending on the pH of the solution and on the metal–ligand molar ratio and the corresponding solid complexes may be obtained (Antolini *et al.*, 1983).

In these complexes the aminoacid molecules adopt different coordination modes: (a) *N,O*-bidentate, e.g., $[Cu(TsglyNO)(H_2O)_3]$, $Na_2[Cu(TsleuNO)_2(H_2O)] \cdot 2H_2O \cdot CH_3OH$ (Antolini *et al.*, 1988), $[PipdH_2][Cu(Ts\text{-}DL\text{-}alaNO)_2 \cdot H_2O$ (Antolini *et al.*, 1985); (b) *N,O*-bidentate, carboxylate bridging and *O*-sulphonyl bridging, e.g., $[Cu(Bs\text{-}DL\text{-}alaNO)(H_2O)_2]_n \cdot nH_2O$ (Chaudhuri, 1984); (c) *N,O*-bidentate, carboxylate bridging, e.g., $[Cu(Ts\text{-}DL\text{-}alaNO)(H_2O)_2]_n \cdot nH_2O$ (Antolini *et al.*, 1985); (d) *N, O*-bidentate and *O*-sulphonyl bridging, e.g., $K_4[Cu_2(TsglyNO)_4]$ (Antolini *et al.*, 1983). These behaviors, nearly ineffective on the features of IR spectra can be revealed by crystal structure analysis; then in order to obtain a deeper insight on the binding ability of this class of ligands we report here the crystal and molecular structure of Cu(II)-*N*-benzenesulphonylglycine complexes of empyrical formulae: $Cu(BsglyNO) \cdot 3H_2O$ and $K_2[Cu(BsglyNO)_2]$.

Experimental

Preparation of (triaqua-N-benzenesulphonylglycinato-NO)copper (II) (I)

4 mmol of BsglyH and 2 mmol of copper (II) acetate monohydrate were dissolved in 50 ml of H_2O at 50°C. The pale-blue solution was filtered and cooled at room temperature (25°C) and after few days pale-blue crystals of complex (I) were separated. (Found: C 29.00, H 4.00, N 4.15, S 9.70%. Calc. for $C_8H_{13}CuNO_7S$: C 29.00, H 4.00, N 4.25, S 9.70%).

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Preparation of [bis(N-benzenesulphonylglycinato-NO)cuprate(II)] dipotassium (II)

The pH of a solution containing BsglyH and copper (II) acetate monohydrate in the ligand-metal molar ratio of 2 : 1 is corrected to 11.5 with aqueous KOH; by evaporation in air at room temperature deep blue crystals of the complex (II) were obtained. (Found C 33.60, H 2.40, N 4.90, S 10.70%. Calc. for $C_{16}H_{14}CuK_2N_2O_8S_2$: C 33.80, H 2.50, N 4.95, S 11.30%).

Physical measurements

Electronic spectra were obtained with a Varian Cary 2300 and infrared spectra a Brucker FT-IR IFS113v spectrophotometers as KBr pellets.

X-ray data collection and structure determination

The most relevant crystal data for both compounds are quoted in Table 1. Cell dimensions were measured by diffractometry with an ''on line'' single-crystal Siemens AED diffractometer and refined by least squares procedure using θ values of 15 high-angle reflections accurately measured—one reflection was measured after every 50 reflections as a check on alignment and on the crystal and instrument stability. After the usual Lorentz and polarization correction, the structure amplitudes were put on absolute scale by least squares.

Correction for absorption was applied only to the data of the complex (II) (absorption correction, min.–max. 0.95–1.05), as the crystal of compound (I) presented a regular shape. For (I) hydrogen atoms, except those of water molecules, were located in a ΔF synthesis and introduced in the final structure factor calculation, the final R index was 0.0596.

In (II) the hydrogen atoms, located in a ΔF synthesis were refined isotropically. The final R index was 0.0446. The final values of the positional parameters are given in Table 2 and 3, respectively. The neutral atom scattering factors were taken from the International Tables, structural calculations were performed by the SHELX program system (Sheldrick, 1976), distance,

Table 1. Experimental data for the crystallographic analyses

Formula		$C_8H_{13}CuNO_7S$	$C_{16}H_{14}CuK_2N_2O_8S_2$
M		330.8	596.2
Space group		$P2_1/c$	Pbca
a, Å		12.736(4)	23.333(8)
b, Å		10.292(3)	10.508(4)
c, Å		10.402(3)	16.989(5)
α, °		90	90
β, °		109.41(2)	90
γ, °		90	90
U, Å^3		1286(1)	4165(1)
Z		4	8
D_c, g cm^{-3}		1.71	1.81
D_m, g cm^{-3}		1.69	1.78
Reflections for	number	15	15
lattice parameters	θ range	62.7–69.8	24–40
$F(000)$		676	2296
Temperature, K		20	20
Diffractometer		SiemensAED	SiemensAED
Crystal size, mm		0.59 × 0.45 × 0.59	0.45 × 0.23 × 0.68
μ, cm^{-1}		41.25	74.13
Scan speed, °min^{-1}		3	4
Scan width, °		$1.3 + 0.35 \tan\theta$	$1.2 + 0.35 \tan\theta$
θ range, °		3–70	3–70
Scan mode		$\omega - 2\theta$	$\omega - 2\theta$
No. of refl. meas.		2733	3192
No. of refl. used in the ref. ($I > 3\sigma(I)$)		2014	1962
No. of refined parameters		182	336
Absorption correction (min.-max.)		—	0.95–1.05
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$		0.0596	0.0446
$R' = [\Sigma w(\Delta F^2)/\Sigma wF_o^2]^{1/2}$		0.0618	0.0532
w, g in $w = k/[\sigma^2(F_o) + gF_o^2]$		1, 17.2×10^{-3}	0.5416, 5.44×10^{-3}
Max., min. height in final ΔF map, eÅ^{-3}		0.35, −1.17	0.20, −0.40

angles, and mean planes by PARST (Nardelli, 1983) and drawings were carried out by ORTEP (Johnson, 1965). The absorption correction was performed using ABSORB program (Ugozzoli, 1983). Final atomic co-ordinates are quoted in Tables 2 and 3 for (I) and (II), respectively, those of hydrogen atoms are quoted in the supplementary material.

Analyses

Carbon, hydrogen, nitrogen, and sulphur were analyzed with a Carlo Erba Model 1106 by Mr. G. Goldoni.

Description of the structures

A perspective view of the molecules with the numbering scheme are reported in Fig. 1 for compound (I) and in Fig. 2 for compound (II); in Tables 4 and 5 bond distances and angles are reported. In the complex (I) coordination around the copper is distorted square pyramidal, the benzenesulphonylglycine acting as bidentate via deprotonated nitrogen atom and a carboxylic oxygen in the basal plane and three water molecules, one of which at the apex of the pyramid. The coordination polyhedron is a quite regular pyramid, being the four equatorial atoms coplanar. The copper atom lies out of this plane 0.21 Å toward the apical

Table 2. Complex I: Atomic coordinates (× 10^4) and equivalent isotropic thermal parameters ($Å^2$ × 10^4) (one third trace of the diagonalized matrix), with esd's in parentheses

Atom	X/a	Y/b	Z/c	U_{eq}
Cu	4390.1(4)	61.8(4)	−1944.9(5)	283(3)
S	2556.5(6)	1120.9(8)	−670.9(8)	305(3)
O1	4271(2)	−1811(3)	−1884(3)	375(9)
O2	3543(2)	−3451(2)	−1092(3)	368(9)
O3	2332(2)	875(3)	595(3)	472(10)
O4	3076(2)	2378(2)	−743(3)	387(9)
O5	5693(2)	−230(3)	−2595(3)	357(9)
O6	4781(3)	1880(3)	−1622(3)	426(10)
O7	3333(3)	276(3)	−4172(3)	463(10)
N	3322(3)	27(2)	−948(4)	309(11)
C1	3624(3)	−2280(3)	−1280(3)	284(10)
C2	2929(3)	−1305(3)	−832(4)	363(13)
C3	1249(3)	1133(4)	−1980(4)	371(12)
C4	1135(3)	1766(4)	−3171(4)	475(13)
C5	126(4)	1773(5)	−4231(5)	691(20)
C6	−761(4)	1096(6)	−4080(6)	729(21)
C7	−646(4)	434(7)	−2894(8)	811(28)
C8	352(4)	439(5)	−1834(5)	572(18)

Table 3. Complex II: Atomic coordinates (× 10^4) and equivalent isotropic thermal parameters ($Å^2$ × 10^4) (one third trace of the diagonalized matrix), with esd's in parentheses

Atom	X/a	Y/b	Z/c	U_{eq}
Cu	689.3(2)	5060.3(5)	7583.7(3)	212(2)
K1	−456.4(4)	5996.2(8)	6270.6(5)	312(3)
K2	−498.7(4)	4010.1(8)	8544.5(5)	281(3)
S1	1023.0(4)	5495.2(9)	5775.4(5)	235(3)
S2	893.5(4)	4501.1(9)	9378.7(5)	227(3)
O1	593(2)	3248(3)	7711(2)	351(10)
O2	648(2)	1392(3)	7091(2)	374(10)
O3	749(1)	6724(3)	5793(2)	332(9)
O4	1015(1)	4815(3)	5033(2)	337(9)
O5	727(2)	6875(3)	7488(2)	351(10)
O6	671(2)	8691(3)	8143(2)	443(11)
O7	564(1)	3342(3)	9422(2)	327(9)
O8	970(1)	5167(3)	10121(2)	313(9)
N1	756(1)	4642(3)	6456(2)	231(9)
N2	640(1)	5415(3)	8729(2)	252(10)
C1	685(2)	2567(4)	7093(2)	281(12)
C2	860(2)	3269(4)	6353(3)	306(12)
C3	1759(2)	5731(4)	6005(2)	282(12)
C4	1928(2)	6680(5)	6524(3)	418(15)
C5	2500(2)	6789(6)	6719(4)	524(19)
C6	2899(2)	5939(6)	6418(4)	515(19)
C7	2728(2)	5007(6)	5911(4)	578(21)
C8	2162(2)	4896(5)	5704(4)	469(17)
C9	682(2)	7529(4)	8129(2)	294(12)
C10	653(2)	6782(4)	8894(3)	300(13)
C11	1597(2)	4050(4)	9075(3)	287(12)
C12	1910(2)	4813(5)	8574(3)	450(16)
C13	2478(2)	4509(6)	8415(4)	572(20)
C14	2731(3)	3474(6)	8764(4)	594(21)
C15	2412(3)	2700(6)	9228(4)	709(25)
C16	1838(2)	2984(5)	9400(3)	515(18)

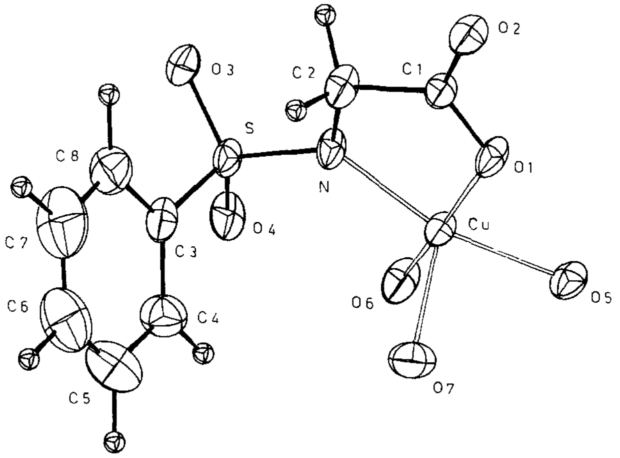

Fig. 1. Perspective view of the complex (I).

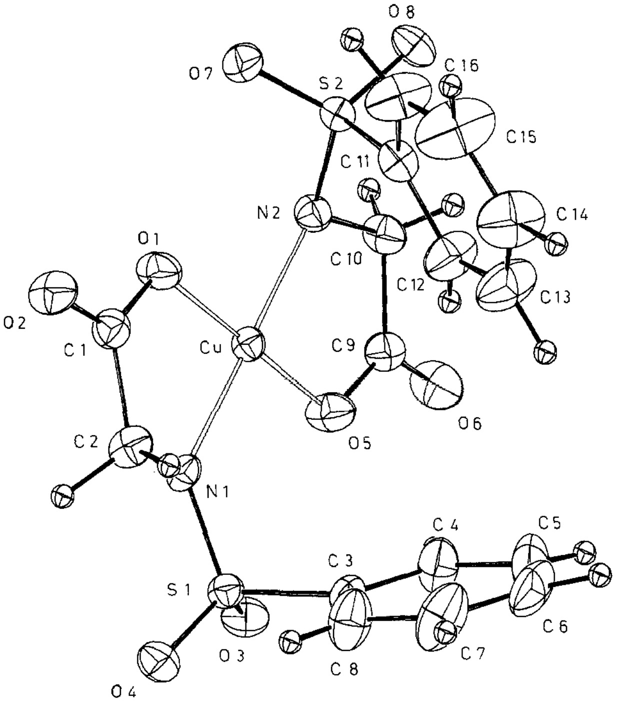

Fig. 2. Perspective view of the complex (II).

Table 4. Complex I

Bond distances (angstrom)			
Cu—O1	1.936(3)	Cu—O5	2.012(3)
Cu—O6	1.936(3)	Cu—O7	2.270(3)
Cu—N	1.966(4)	S—O3	1.459(3)
S—O4	1.467(2)	S—N	1.578(3)
S—C3	1.766(3)	O1—C1	1.284(5)
O2—C1	1.232(4)	N—C2	1.478(4)
C1—C2	1.511(5)	C3—C4	1.365(6)
C3—C8	1.398(6)	C4—C5	1.387(6)
C5—C6	1.380(8)	C6—C7	1.374(10)
C7—C8	1.379(7)		
Bond angles (degrees)			
O7—Cu—N	105.1(1)	O6—Cu—N	96.3(1)
O6—Cu—O7	96.6(1)	O5—Cu—N	165.3(1)
O5—Cu—O7	87.0(1)	O5—Cu—O6	90.5(1)
O1—Cu—N	83.6(1)	O1—Cu—O7	95.9(1)
O1—Cu—O6	167.1(1)	O1—Cu—O5	86.8(1)
N—S—C3	110.3(2)	O4—S—C3	106.3(2)
O4—S—N	107.7(2)	O3—S—C3	106.2(2)
O3—S—N	111.1(2)	O3—S—O4	115.2(2)
Cu—O1—C1	117.4(2)	Cu—N—S	131.4(2)
S—N—C2	113.6(3)	Cu—N—C2	111.9(2)
O1—C1—O2	123.2(3)	O2—C1—C2	120.8(3)
O1—C1—C2	116.0(3)	N—C2—C1	109.9(3)
S—C3—C8	120.5(3)	S—C3—C4	119.5(3)
C4—C3—C8	119.9(4)	C3—C4—C5	121.0(4)
C4—C5—C6	119.0(5)	C5—C6—C7	120.3(5)
C6—C7—C8	120.8(6)	C3—C8—C7	119.0(5)

Table 5. Complex II

Bond distances (angstrom)			
Cu—O1	1.930(3)	Cu—O5	1.916(3)
Cu—N1	1.972(3)	Cu—N2	1.984(4)
S1—O3	1.441(3)	S1—O4	1.450(3)
S1—N1	1.590(3)	S1—C3	1.778(4)
S2—O7	1.442(3)	S2—O8	1.453(3)
S2—N2	1.579(4)	S2—C11	1.786(4)
O1—C1	1.289(5)	O2—C1	1.237(5)
O5—C9	1.292(5)	O6—C9	1.221(5)
N1—C2	1.474(5)	N2—C10	1.464(5)
C1—C2	1.514(6)	C3—C4	1.389(7)
C3—C8	1.384(7)	C4—C5	1.380(8)
C5—C6	1.387(8)	C6—C7	1.364(9)
C7—C8	1.372(8)	C9—C10	1.519(6)
C11—C12	1.379(7)	C11—C16	1.368(7)
C12—C13	1.389(7)	C13—C14	1.372(9)
C14—C15	1.354(9)	C15—C16	1.404(9)
Bond angles (degrees)			
N1—Cu—N2	177.6(1)	O5—Cu—N2	84.2(1)
O5—Cu—N1	97.8(1)	O1—Cu—N2	93.9(1)
O1—Cu—N1	84.2(1)	O1—Cu—O5	175.6(2)
N1—S1—C3	107.3(2)	O4—S1—C3	105.7(2)
O4—S1—N1	110.4(2)	O3—S1—C3	107.5(2)
O3—S1—N1	108.4(2)	O3—S1—O4	117.0(2)
N2—S2—C11	107.8(2)	O8—S2—C11	105.4(2)
O8—S2—N2	111.1(2)	O7—S2—C11	106.3(2)
O7—S2—N2	110.4(2)	O7—S2—O8	115.4(2)
Cu—O1—C1	115.9(3)	Cu—O5—C9	117.0(3)
Cu—N1—S1	127.7(2)	S1—N1—C2	113.6(3)
Cu—N1—C2	110.2(3)	Cu—N2—S2	123.4(2)
S2—N2—C10	117.0(3)	Cu—N2—C10	111.8(3)
O1—C1—O2	123.0(4)	O2—C1—C2	120.2(4)
O1—C1—C2	116.8(4)	N1—C2—C1	109.5(3)
S1—C3—C8	119.2(4)	S1—C3—C4	120.9(3)
C4—C3—C8	119.8(4)	C3—C4—C5	119.1(5)
C4—C5—C6	120.5(5)	C5—C6—C7	120.0(5)
C6—C7—C8	120.2(6)	C3—C8—C7	120.4(5)
O5—C9—O6	123.3(4)	O6—C9—C10	120.0(4)
O5—C9—C10	116.7(4)	N2—C10—C9	110.1(3)
S2—C11—C16	118.6(4)	S2—C11—C12	120.7(4)
C12—C11—C16	120.5(4)	C11—C12—C13	119.4(5)
C12—C13—C14	120.5(5)	C13—C14—C15	119.4(5)
C14—C15—C16	121.1(6)	C11—C16—C15	118.8(5)

oxygen and the angles between the Cu—O7 line with the normal to the basal plane 9.1(1)°. The coordination is effectively 4 + 1, the shortest contact with the Cu atom on the opposite side to O7 involves a centrosymmetrically related nitrogen atom, Cu · · · N(1 $-x$, $-y$, $-z$) 3.424(3) Å. The five-membered chelation ring forms with the benzene ring an angle of 86.2(1)° and one of 42.6(1)° with the sulphonic group. This type of coordination is very similar to that found in the corresponding tosylglycinate complex, $[Cu(TsglyNO)(H_2O)_3]$, bond distances are also in good agreement. Packing is determined by O · · · O contacts, which can be considered as hydrogen bonds quoted in Table 6.

In $K_2[Cu(BsglyNO)_2]$, the copper atom is surrounded by two carboxylic oxygen and two amide nitrogen atoms belonging to two different aminoacid molecules. In this way coordination around the copper results square planar tetrahedrally distorted with N1 −0.036(3), N2 −0.043(3) O1 0.049(4), O5 0.048(4) Å out of the mean plane. It is worth of note the different arrangement of this complex with respect to the analogous tosylglycinate, where dimeric species were present. In this case the structure consists of $[Cu(BsglyNO)_2]^{2-}$ monomeric units. The presence of the phenyl group sterical hindrance can be considered as responsible of the shortening of the Cu—O5 and Cu—N1 distance, with respect to the chemically equivalent ones.

Potassium ions, K1 at 3.618(1) Å and K2 at 3.401(1) Å from the copper atom, are surrounded within 3.1 Å the first by six atoms at the corners of a distorted trigonal prism, the second by seven oxygen atoms in a highly distorted pentagonal bipyramidal arrangement, the distances range from 2.665(3) to 3.024(3) Å (sum of the ionic radii 2.73 Å). The potassium ions are bridging by two carboxylic oxygens, the bridges being linked to form chains where the potassium ions are alternate as follows: $K2^{i}$ · · · K1 · · · K2 · · · $K1^{ii}$ ($i = -x, 1/2 + y, 3/2 - z$; $ii = -x, y - 1/2, 3/2 - z$); $K2^{i}$ · · · K1 3.885(2); K1 · · · K2 4.392(2) Å. The environment of the potassium ions determinate the packing, which is completed by van der Waals interactions quoted in Table 7. Packing for the two complexes are reported

Table 6. Intermolecular contacts less than 3.5 Å for (I) and (II)

(I)			
O5 · · · $O2^{i}$	2.654(4)	O5 · · · $O3^{iii}$	2.761(4)
O6 · · · $O1^{i}$	2.634(5)	O6 · · · $O5^{i}$	3.091(4)
O7 · · · $O2^{ii}$	2.818(4)	O7 · · · $O4^{iv}$	2.873(4)

i $1 - x, 1/2 + y, -z - 1/2$
ii $x, -1/2 - y, z - 1/2$
iii $1 - x, -y, -z$
iv $x, 1/2 - y, z - 1/2$

(II)			
O1 · · · $O5^{i}$	3.418(5)	O1 · · · $O6^{i}$	3.319(5)
O2 · · · $O6^{ii}$	3.327(5)	O2 · · · $O6^{ii}$	3.355(4)
O3 · · · $O8^{iii}$	3.450(4)		

i $-x, y - 1/2, 3/2 - z$
ii $x, y - 1, z$
iii $x, 3/2 - y, z - 1/2$

Table 7. Potassium atoms environments

K1—$O1^{i}$	2.948(3)	K2—O7	2.977(3)
K1—$O2^{i}$	2.948(3)	K2—$O2^{i}$	2.749(3)
K1—$O4^{ii}$	2.849(3)	K2—$O3^{iii}$	2.717(3)
K1—$O6^{iii}$	2.667(3)	K2—$O5^{iii}$	2.898(3)
K1—$O7^{i}$	2.743(3)	K2—$O6^{iii}$	2.914(3)
K1—O3	3.024(3)	K2—$O8^{iv}$	2.665(3)
		K2—O1	3.016(3)

(*i*) $-x, 1/2 + y, 3/2 - z$
(*ii*) $-x, 1 - y, 1 - z$
(*iii*) $-x, -1/2 + y, 3/2 - z$
(*iv*) $-x, 1 - y, 2 - z$

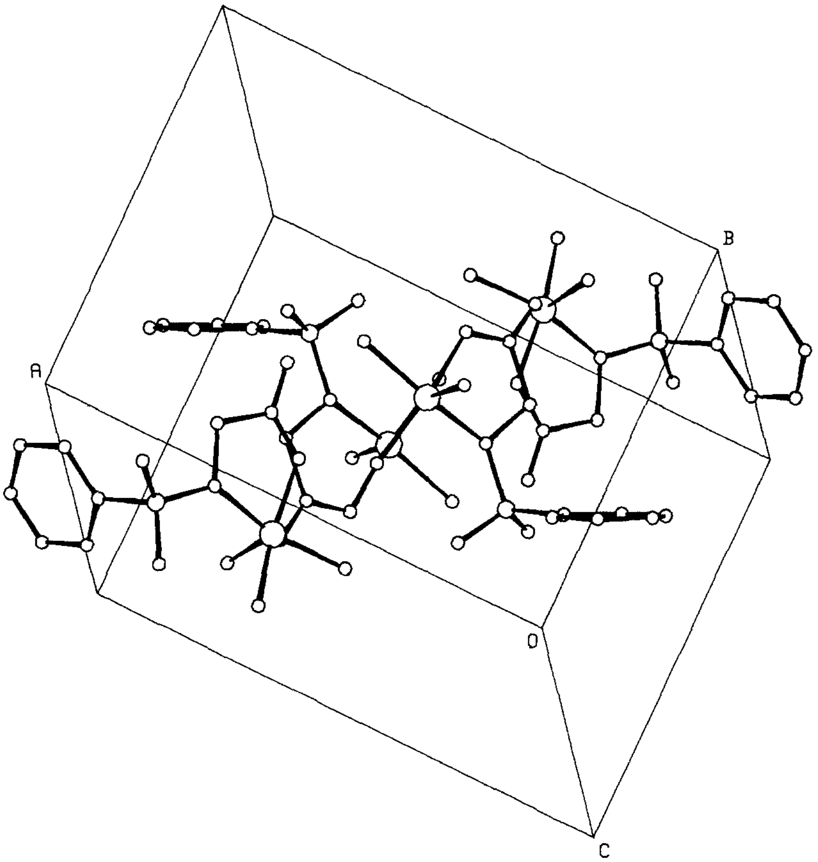

Fig. 3. Packing of complex (I).

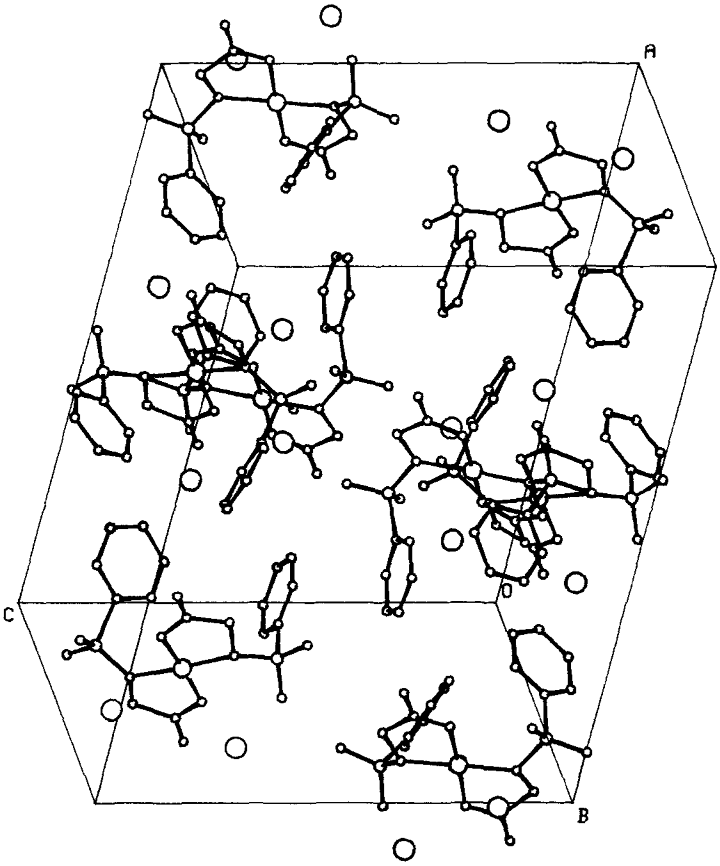

Fig. 4. Packing of complex (II).

Table 8. Selected infrared bands of solid compounds (cm^{-1})

	ν(NH)	$\nu(COO)_{as}$	$\nu(COO)_s$	$\nu(SO)_{as}$	$\nu(SO)_s$	ν(SN)
BsglyH	3315 vs	1729 vs	1248 vs	1318 vs	1159 1131 vs	868 s
$[Cu(BsglyNO)(H_2O)_3]^a$		1617 vs	1392 vs	1241 vs	1135 1113 vs	979 s
$K_2[Cu(BsglyNO)_2]$		1636 1620 vs	1383 1370 vs	1287 1260 vs	1140 1114 1103	982 s 931

[a] $\nu(OH)_{as}$ = 3516, 3439 ms.

in Figs. 3 and 4, where appears the reciprocal orientation of the phenyl rings and of hydrophilic and hydrophobic moieties of the aminoacids. The most significant absorption bands are reported on Table 8.

Spectroscopic results

The d-d band maximum position (13800 cm^{-1}) of the aqua-complex is strictly similar to that of the isostructural N-tosylglycinate analogous (II); for $K_2[Cu(BsglyNO)_2]$ the d-d maximum (17400 sh, 14700 cm^{-1}) is also consistent with an essentially square-planar CuN_2O_2 chromophore although the long Cu · · · K contacts may be responsible for the decrease of absorption energy respect to the $[PipdH_2][Cu(Ts\text{-}DL\text{-}alaNO)_2 \cdot H_2O$ complex.

In the infrared spectra (supplementary material) the shift of band maxima assigned to sulphonamide group (asymmetric and symmetric $\nu(SO_2)$, ν(SN) and the disappearance of ν(NH) are in line with the presence of a deprotonated and metal coordinated nitrogen atom (II). In addition, for the $[Cu(BsglyNO)(H_2O)_3]$ complex, all the significant band are nearly coincident with those of the isostructural $[Cu(TsglyNO)(H_2O)_3]$ complex (II).

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Thermal parameters, hydrogen atom coordinates and Structure factor data have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK, as supplementary publication No. 63142 (55 pages).