Inorganica Chimica Acta, 93 (1984) 61–66

Imidazole-Containing Ternary Complexes of N-benzyloxycarbonyl-aminoacids. Crystal and Molecular Structure of Bis(N-benzyloxycarbonyl-alaninato)bis-(N-methylimidazole)copper(II) Ethanol Solvate

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Received April 12, 1984

Abstract

Mixed ligand complexes of the type Cu(Z-aminoacidato)$_2$(B$_2$) (Z = benzyloxycarbonyl group, Z-aminoacidate = Z-glycinate (Zgly), Z-alaninate (Zala), Z-valinate (Zval), Z-leucinate (Zleu) ion, B = imidazole (Im), N-methylimidazole (MeIm)) were synthesized and characterized by means of electronic, infrared and EPR spectroscopies. For one of them, bis-(Z-alaninato)bis(N-methylimidazole)copper(II) ethanol solvate, the crystal and molecular structure was also determined by the single crystal X-ray diffraction method. The complex crystallizes in the monoclinic space group $P2_1/c$, with cell dimensions a = 11.1119(6), b = 18.8398(7), c = 8.9652(5) Å, β = 105.380(2)° and Z = 2. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares to an R value of 0.045. The complex has square-planar coordination *via* two centrosymmetric carboxylic oxygens and two N-methylimidazole nitrogens. The second carboxylate oxygen is 2.731(5) Å from the copper atom in an 'out of plane' position. Packing is mainly determined by hydrogen bondings between amide nitrogen and amide carboxyl oxygen. Electronic, infrared and EPR spectra are consistent with this type of coordination geometry for anhydrous complexes, while for hydrate complexes are suggestive of tetragonal bipyramidal geometry.

Introduction

Our interest in the structural, spectroscopic and magnetic properties of simple metal(II) complexes with N-protected aminoacids, where the protecting group was an acetyl [1], benzoyl [2] or 4-toluenesulfonyl [3] (hereafter abbreviated as tosyl) group, derives from the fact that they may supply information about the bonding characteristics of protein-like donor molecules toward metal ions. In these complexes, the ligands have invariably been found to coordinate through the carboxylate group (for the Cu(II)–tosyl-aminoacids complexes only at pH 5) and owing to the weak coordination ability of the $-COO^-$ group they must easily react with strong donor molecules such as aliphatic and aromatic amines. As a consequence, a coordination geometry change, such as function of pK_A and binding mode of amines, has been found.

In particular we have focused our investigations on the imidazole-containing copper(II)–N-protected aminoacids complexes as they are naturally occurring systems, implicated in the storage and transport of metal ions themselves and of active substances through membranes [4, 5].

In this paper we report a study on ternary copper(II)–imidazole complexes with N-benzyloxycarbonyl-(hereafter abbreviated as Z-) aminoacids [6], and for one of them the bis(Z-alaninato)bis(N-methylimidazole)copper(II) ethanol solvate the crystal and molecular structure has also been determined. The reason for the choice of this protecting group also depends on the fact that, despite the direct implication of Z-glycine as activator or inhibitor of hydrolysis of esthers and longer peptides, in reaction catalyzed by the CPA [7], the crystallographic observations on CPA–Z-glycine and metal(II)–Z-glycinate systems are lacking and the binding arrangement for the action of Z-glycine has only been suggested by model building.

Experimental

All chemicals were reagent grade and used as received.

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0020-1693/84/$3.00

TABLE I. Crystal Data.

Molecular Formula	$C_{32}H_{42}CuN_6O_9$
Mol wt	718.27
a, Å	11.1119(6)
b, Å	18.8398(7)
c, Å	8.9652(5)
β, deg	105.380(2)
V, Å^3	1809.6(2)
d_{meas}, g cm^{-3}	1.30
Z	2
d_{calc}, g cm^{-3}	1.32
Space group	$P2_1/c$
Crystal dimensions, mm	0.22 × 0.22 × 0.29
Radiation (λ, Å)	Cu-Kα (λ = 1.54178) (Ni-filtered)
2θ limits, deg	6–120
Scan technique	ω–2θ
Temp., °C	20
Abs coeff., cm^{-1}	13.02
F(000), electrons	754
Unique data used ($I > 2\sigma(I)$)^a	1542
No. of variables	261
R	0.0448
R_w^{b}	0.0502
g	3.4 × 10^{-3}

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

Preparation of the Complexes [Cu(Z-aminoacidato)$_2$B$_2$], Z-aminoacidate = Z-glycinate (Zgly), Z-valinate (Zval), and Z-leucinate (Zleu) Anion and B = Imidazole (Im) and N-methylimidazole (MeIm), and bis(Z-alaninato)bis(N-methylimidazole)copper(II) ethanol solvate, [Cu(Zala)$_2$(MeIm)$_2$]·EtOH

All the compounds were prepared by mixing the simple [Cu(Z-aminoacidato)$_2$·H$_2$O] (Z-aminoacidate = Zgly, Zval, Zleu) complexes and [Cu(Zala)$_2$] [22] with an ethanolic or methanolic solution of Im or MeIm in a metal:amine molar ratio of 1:2. By evaporating these solutions at room temperature (~20 °C), after 12 h, violet or blue–violet crystals separated.

[Cu(Zly)$_2$(Im)$_2$·H$_2$O]: *Anal.* Calcd for $C_{26}H_{30}CuN_6O_9$: C, 49.22; H, 4.77; N, 13.26; H$_2$O, 2.84. Found: C, 49.82; H, 4.63; N, 13.60; H$_2$O, 2.78.

[Cu(Zala)$_2$(Im)$_2$·0.5H$_2$O]: *Anal.* Calcd. for $C_{28}H_{33}CuN_6O_{8.5}$: C, 51.47; H, 5.18; N, 12.87; H$_2$O, 1.38. Found: C, 51.32; H, 5.11; N, 12.99; H$_2$O, 1.30.

[Cu(Zval)$_2$(Im)$_2$·H$_2$O]: *Anal.* Calcd. for $C_{32}H_{42}CuN_6O_9$: C, 53.49; H, 5.90; N, 11.71; H$_2$O, 2.51. Found: C, 54.17; H, 5.97; N, 11.91; H$_2$O, 2.45.

[Cu(Zleu)$_2$(Im)$_2$]: *Anal.* Calcd. for $C_{34}H_{44}CuN_6O_8$: C, 56.05; H, 6.09; N, 11.55.. Found: C, 56.13; H, 5.94; N, 11.39.

[Cu(Zgly)$_2$(MeIm)$_2$]: *Anal.* Calcd. for $C_{28}H_{42}CuN_6O_8$: C, 52.19; H, 5.01; N, 13.05. Found: C, 51.90; H, 5.08; N, 12.88.

[Cu(Zala)$_2$(MeIm)$_2$]·EtOH: *Anal.* Calcd. for $C_{32}H_{42}CuN_6O_9$: C, 53.36; H, 5.87; N, 11.70; EtOH, 6.47. Found: C, 53.56; H, 5.89; N, 11.94; EtOH, 6.39.

[Cu(Zval)$_2$(MeIm)$_2$]: *Anal.* Calcd. for $C_{34}H_{44}CuN_6O_8$: C, 56.05; H, 6.09; N, 11.55. Found: C, 55.72; H, 6.16; N, 11.53.

[Cu(Zleu)$_2$(MeIm)$_2$]: *Anal.* Calcd. for $C_{36}H_{48}CuN_6O_8$: C, 57.15; H, 6.40; N, 11.12. Found: C, 55.97; H, 6.60; N, 10.86.

Physical Measurements

The electronic, EPR and infrared spectra, the magnetic measurements and the thermogravimetric analysis were performed as described in refs. [8] and [9].

X-ray Data Collection and Structure Determination

The most relevant crystal data are summarized in Table I. Cell dimensions, measured by diffractometry with an 'on line' single crystal automated Siemens AED diffractometer, were refined by least-squares using θ values of 15 high-angle reflections accurately measured. During the total data collection using the same diffractometer and CuKα radiation one reflection was measured after every 50 reflections as a check on the alignment of the crystal and instrument stability. The individual reflection profile was analyzed as indicated in ref. [10]. All data were corrected for Lorentz and polarization effects, but not for absorption, since the absorption coefficient was very small (μR = 0.14). 1542 reflections from 2697 collected, for which $I > 2\sigma(I)$ were considered as observed and used in the structure determination. The structure was solved by conventional Patterson and Fourier methods and refined isotropically by full-matrix least-squares calculation to an R index of 9.5%. A difference Fourier map calculated at this stage showed four peaks astride a center of symmetry. The shape of this was consistent with an ethanol solvent molecule trapped in the lattice and disordered in two orientations with the symmetry center at the middle of the C–C bond. To allow for this, two atoms, one oxygen with occupancy 0.5 and one carbon with occupancy 1, lead the R index to 6.5%. The final refinement carried out anisotropically for copper atom and N-methylimidazole and aminoacid molecules, isotropically for hydrogen atoms, located in the ΔF map, and for ethanol, leads the R index to 0.0045 (R_w = 0.050). The hydrogen atoms of the ethanol molecule are not located. The atomic scattering factors used,

TABLE II. Fractional Atomic Coordinates (×10^4).

	x/a	*y/b*	*z/c*
Cu	0(0)	0(0)	0(0)
O(1)	223(4)	1017(2)	511(5)
O(2)	2043(5)	615(2)	1956(6)
O(3)	21(4)	1918(2)	3749(5)
O(4)	−1109(4)	2730(2)	2085(5)
O(et)	4645(15)	4470(8)	6485(20)
N(1)	672(5)	2349(3)	1733(7)
N(2)	−742(5)	−148(2)	1751(6)
N(3)	−1564(5)	80(3)	3675(6)
C(1)	1286(7)	1098(3)	1439(7)
C(2)	1706(6)	1857(3)	1923(8)
C(3)	2612(8)	2113(5)	1039(12)
C(4)	−111(6)	2298(3)	2605(8)
C(5)	−1993(8)	2760(5)	3013(10)
C(6)	−3132(7)	3096(4)	2052(9)
C(7)	−3848(9)	2736(5)	784(11)
C(8)	−4923(10)	3050(7)	−169(13)
C(9)	−5250(9)	3716(7)	120(14)
C(10)	−4566(11)	4091(6)	1378(14)
C(11)	−3456(8)	3779(5)	2338(10)
C(12)	−1140(7)	353(7)	2531(9)
C(13)	−2127(11)	479(5)	4725(12)
C(14)	−1409(9)	−626(4)	3625(10)
C(15)	−902(9)	−768(4)	2452(9)
C(et)	4492(13)	4742(7)	4999(18)

corrected for anomalous dispersion, were taken from the 'International Tables' [11].

Seven reflections (2 0 2, −2 5 2, 3 0 4, 1 0 0, 0 2 0, 3 2 0, −1 2 1) were excluded from the final refinement, as they had been affected by extinction or counting errors.

All the calculations were performed by using the CYBER 7600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Bologna, with the SHELX 76 system of programs [12] and ORTEP plotting program [13].

Final fractional coordinates for non hydrogen atoms are listed in Table II, those for hydrogen atoms are available in the supplementary material.

Analysis

Nitrogen, carbon and hydrogen were analyzed with a C. Erba Model 1106 elemental analyser instrument by Mr. G. Pistoni. The ethanol was determined thermogravimetrically with a Mettler TA3000 instrument.

Results and Discussion

Description of the Structure

Bond distances and angles in the [Cu(Zala)$_2$·(MeIm)$_2$]·EtOH complex are given in Table III, with atoms labelled as in Fig. 1.

TABLE III. Bond Distances (Å) and Angles (deg) with E.s.d.s in Parentheses.

a) In the coordination polyhedron			
Cu–O(1)	1.970(4)	Cu–N(2)	1.977(6)
Cu–O(2)	2.731(5)		
		O(1)–Cu–N(2)	90.3(2)
b) In the ligands			
C(1)–O(1)	1.261(8)	C(8)–C(9)	1.350(19)
C(1)–O(2)	1.242(8)	C(9)–C(10)	1.376(16)
C(1)–C(2)	1.531(8)	C(10)–C(11)	1.430(14)
C(2)–C(3)	1.516(13)	C(6)–C(11)	1.378(12)
C(2)–N(1)	1.451(8)	N(2)–C(12)	1.319(12)
N(1)–C(4)	1.318(10)	N(2)–C(15)	1.360(9)
C(4)–O(3)	1.227(8)	N(3)–C(12)	1.340(11)
C(4)–O(4)	1.355(7)	N(3)–C(13)	1.468(13)
O(4)–C(5)	1.447(11)	N(3)–C(14)	1.344(10)
C(5)–C(6)	1.472(11)	C(14)–C(15)	1.345(14)
C(6)–C(7)	1.380(11)	C(7)–C(8)	1.402(14)
O(1)–C(1)–C(2)	117.5(6)	C(12)–N(2)–C(15)	105.4(6)
O(2)–C(1)–C(2)	116.9(6)	N(2)–C(15)–C(14)	108.9(6)
O(1)–C(1)–O(2)	125.5(6)	C(15)–C(14)–N(3)	107.9(7)
C(3)–C(2)–C(1)	110.1(6)	C(14)–N(3)–C(12)	106.3(7)
C(3)–C(2)–N(1)	110.5(6)	N(2)–C(12)–N(3)	111.5(9)
C(1)–C(2)–N(1)	113.0(6)	C(13)–N(3)–C(12)	126.2(7)
C(2)–N(1)–C(4)	120.7(6)	C(13)–N(3)–C(14)	127.5(7)
N(1)–C(4)–O(3)	125.9(6)	O(3)–C(4)–O(4)	122.9(6)
O(4)–C(5)–C(6)	106.8(7)		

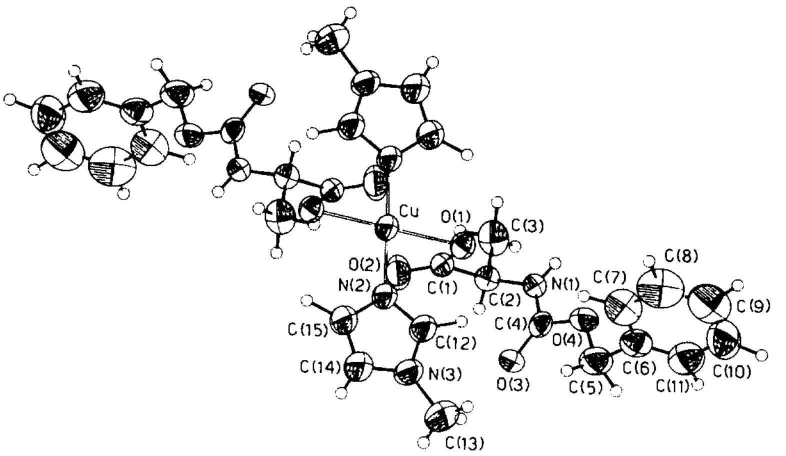

Fig. 1. ORTEP view of the $[Cu(Zala)_2(MeIm)_2] \cdot EtOH$ complex showing the atom numbering and the thermal motion ellipsoids (50%) for non-hydrogen atoms. The hydrogen atoms are represented as spheres of arbitrary radii.

Environment of the Copper Atom

The structure consists of $Cu(Zala)_2(MeIm)_2$ units in which the copper atom, lying on the symmetry center, coordinates two centrosymmetrically disposed aminoacids and N-methylimidazole molecules in a square-planar arrangement. The Z-alaninate ion acts as a simple carboxylate ligand involving in the coordination one oxygen atom of the α-carboxylate group (Cu–O(1) = 1.970(4) Å). The second carboxyl oxygen is 2.731(5) Å from the copper in an 'out of plane' position, the angle between the Cu–O(2) vector and the normal to the equatorial plane being 36.4(2)°. The amide nitrogen is not involved in the coordination to the metal ion. This type of arrangement was found in other ternary copper(II) complexes with heteroaromatic N-bases and N-protected aminoacids, where the protecting group is an acetyl, benzoyl or tosyl group and indicates a negligible effect by different protecting groups on the resultant coordination geometry which seems to be mainly determined by the coordination ability of the amine and by symmetry requirements. This statement is demonstrated by the strict similarity of equatorial copper–ligand bond distances and by the moderate variation of the Cu–O (axial) distance among the complexes in passing from aminoacids with a small substituent, like acetyl, to a bulk substituent, like the Z-group, and going from a weak electron-withdrawing group, like acetyl or benzoyl, to a more acidic group like tosyl. It must also be noted that all these imidazole complexes present a Cu–N-(imidazole) bond length in the range 1.959(5)–1.976(6) Å intermediate between the Cu–N(imidazole) bond distances of 1.95 Å in oligoglycines–Cu^{2+}–imidazole complexes and those of 2.00 Å found in most Cu^{2+}–imidazole complexes [14] due to the expected π-back bonding from Cu^{2+} to the imidazole molecule.

TABLE IV. Most Relevant Torsion Angles.

O(1)–C(1)–C(2)–C(3)	–101.8(7)°
O(2)–C(1)–C(2)–C(3)	75.8(8)
O(1)–C(1)–C(2)–N(1)	22.3(8)
O(2)–C(1)–C(2)–N(1)	–160.1(6)
C(1)–C(2)–N(1)–C(4)	67.8(8)
C(2)–N(1)–C(4)–O(3)	10.0(1.0)
C(2)–N(1)–C(4)–O(4)	–170.4(5)
O(3)–C(4)–O(4)–C(5)	4.0(9)
N(1)–C(4)–O(4)–C(5)	–175.7(6)
C(4)–O(4)–C(5)–C(6)	–165.3(6)
O(4)–C(5)–C(6)–C(7)	68.7(9)
O(4)–C(5)–C(6)–C(11)	–107.3(9)

Z-alaninate Anion

The C^{α}–COO group is planar with the amide nitrogen 0.471 Å out of the mean plane, and is quite orthogonal to the $\mathrm{HN{-}\underset{\underset{O}{\|}}{C}{-}O{-}}$ (dihedral angle of 79.9(2)°), also the $\mathrm{{-}N{-}\underset{\underset{O}{\|}}{C}{-}O{-}}$ (ester) is planar, with the hydrogen atom 0.05(5) Å out of this plane. In the Z-moiety the benzene ring forms an angle of 118.4(2)° with the ester group and 109.6(5)° with the mean plane through O(4), C(5), C(6) atoms. The methylimidazole molecule is orthogonal to the carboxylate group (dihedral angle = 90.4(2)°). Conformation of the N-protected aminoacid can be described by using the torsion angles quoted in Table IV. The Z-group assumes an extended form, the torsion angle being near to 180°, paralleling the behaviour of the same type of ligands [15–18].

Hydrogen Bonding

The crystal packing is presented in Fig. 2. The aminoacid molecules are linked by a rather weak

TABLE V. Room-temperature Electronic (cm^{-1}), Infrared (cm^{-1}), EPR Data and Room-temperature Magnetic Moments (μ_B) for the Complexes.

	1 [Cu(Zgly)$_2$(Im)$_2$·H$_2$O][a]	2 [Cu(Zala)$_2$(Im)$_2$·0.5H$_2$O][a]	3 [Cu(Zval)$_2$(Im)$_2$·H$_2$O][a]	4 [Cu(Zleu)$_2$(Im)$_2$]	5 [Cu(Zgly)$_2$-(MeIm)$_2$]	6 [Cu(Zala)$_2$-(MeIm)$_2$]·EtOH[b]	7 [Cu(Zval)$_2$-(MeIm)$_2$]	8 [Cu(Zleu)$_2$-(MeIm)$_2$]
μ_{eff}	1.86	1.95	1.82	1.89	1.81	1.83	1.92	1.91
d–d band max.	15600	15600	15400	17300	14900sh 17600	15400sh 17600	15600sh 17700	15200sh 17500
$g_\parallel$	2.273	2.234	2.289	2.170	2.273	2.249[c]	2.183	2.257[d]
$g_\perp$	2.116	2.068	2.113	2.066	2.060	2.034	2.053	2.057
ν(NH)	3300msb	3360s	3300msb	3340s	3210ms	3290s	3340ms	3280s
$\nu(OCO)_{asym}^{ester}$	1715vs 1700vs	1715vs 1700sh	1715vs 1700s	1710s 1685vs	1700ms	1695vs 1675vs	1705vs	1710s 1690vs
$\nu(OCO)_{sym}^{ester}$	1270vs 1240vs	1260s 1238vs	1255s 1235s	1260s 1245vs	1265vs 1245vs	1280vs 1255vs	1240s 1230s	1275vs 1250vs
$\nu(OCO)_{asym}^{carbox}$	1590vs	1598vs	1585vs	1610vs	1615vs	1615vs	1585vs	1615vs
$\nu(OCO)_{sym}^{carbox}$	1390vs	1408s	1400vs	1405s	1400vs	1385vs	1395s	1390s

[a] A broad band at 3400 cm^{-1} for complexes 1 and 3 and at 3420 cm^{-1} for 2 is assigned to coordinated water molecule. [b] Two sharp bands at 3670m and 3640m cm^{-1} are assigned to uncoordinated EtOH molecule. [c] $A_\parallel = 189 \times 10^{-4}$ cm^{-1}. [d] $A_\parallel = 200 \times 10^{-4}$ cm^{-1}.

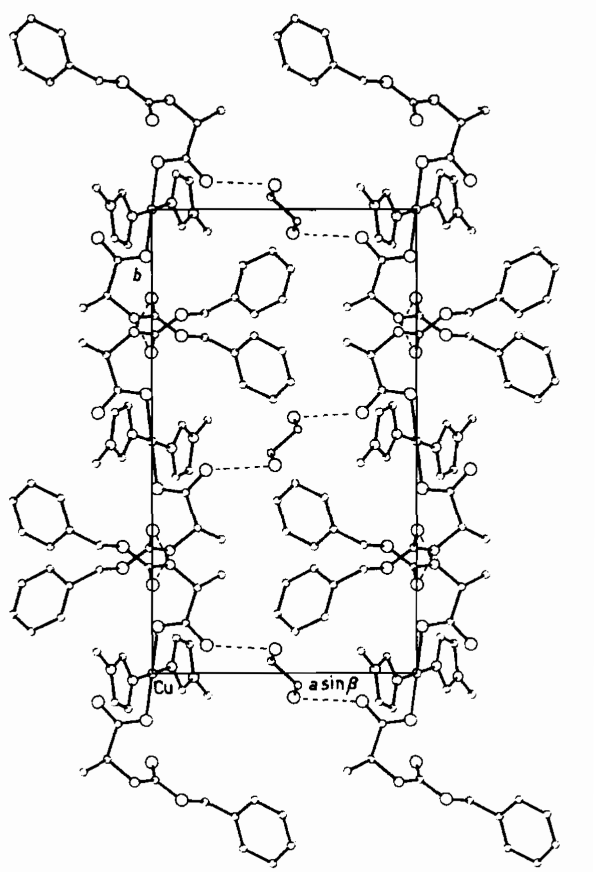

Fig. 2. Projection along *c* axis of the packing of the [Cu(Zala)$_2$(MeIm)$_2$]·EtOH complex.

intermolecular hydrogen bond between the amide nitrogen and amide carboxyl oxygen atoms of the adjacent molecule: N(1)···O(3)^i = 2.926(7) Å (i = x, ½ – y, z + ½) [N(1)–H(5) = 0.79(5) Å, H(5)···O(3)^i = 168(5)°].

The ethanol molecule joins two centrosymmetric molecules of the complex with a contact O(et)··· O(2)^i = 3.03(2) Å (i = x, ½ – y, ½ + z) which involves the uncoordinated carboxyl oxygen. In this way the hydrophobic regions of the complex are connected along the *b* axis *via* N–H···O and along *a* axis *via* O···O bonds. The molecular arrangement in the crystal is completed by van der Waals contacts involving the hydrophobic region of the aminoacid.

Magnetic and Spectroscopic Results

All the complexes present 'normal' room-temperature solid magnetic moments for an orbitally non-degenerate ground state (Table V).

The room-temperature electronic spectrum (Table V) of the structurally known [Cu(Zala)$_2$(MeIm)$_2$]·EtOH complex presents bands at 15900sh and 17600 cm^{-1} and EPR parameters $g_\parallel$ = 2.249 and $g_\perp$ = 2.034 which are in the range found for the other structurally known bis(N-protected aminoacidato)bis(imidazole)copper(II) complexes (spectral range of d–d band maximum = 17500–18200 cm^{-1}; $g_{\parallel}$ = 2.208, $g_{\perp}$ = 2.050) with square planar CuN_2O_2 chromophore, thus confirming that the ligand field strength of N-protected aminoacids is nearly independent of the substituent group on the nitrogen atom. So we may reasonably propose, also for the complexes, 4, 5, 7 and 8 of Table V, the same type of coordination geometry, while for the 1–3 complexes the electronic and EPR data allow us to suggest a tetragonal bipyramidal geometry with CuN_2O_4 chromophore arising from imidazole nitrogen, carboxyl oxygen and water oxygen atoms as indicated by infrared spectra (see below).

In the infrared spectra the absorption frequencies of functional groups (NH, OCO(carboxylic), OCO(ester)) are close to those found in the spectrum of the $[Cu(Zala)_2(MeIm)_2]\cdot EtOH$ complex indicating that the coordination of the carboxylate group is essentially monodentate, the NH and OCO(ester) groups are uncoordinated to the copper atom and the differences are due to hydrogen bondings. In the spectra of complexes 1–3 a broad weak band is present at ~3400 cm^{-1}, attributed to a coordinated water molecule, so providing an explanation for the tetragonal bipyramidal geometry assigned on the basis of electronic spectra.

Acknowledgements

The authors are grateful to the Centro Strumenti of the University of Modena for recording the infrared spectra and the Ministero della Pubblica Istruzione of Italy for financial support.

Supplementary Material

A list of complete structure factors, positional parameters for hydrogen atoms, bond distances involving hydrogen atoms, anisotropic thermal parameters (isotropic for EtOH) and planarity analyses (14 pp.).

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