Ternary Complexes of Copper(II) with *N*-Protected Amino-acids and *N*-Methylimidazole. Crystal and Molecular Structures of Bis(*N*-acetyl-α-alaninato)bis(*N*-methylimidazole)copper(II) Dihydrate

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Ternary complexes of the type $[CuL_2(mim)_2]$ [L = *N*-acetyl-α-, *N*-benzoyl-α-, *N*-acetyl-β-, or *N*-benzoyl-β-alaninate(1−); mim = *N*-methylimidazole], $[CuL_2(mim)_2]\cdot H_2O$ (L = benzoylglycinate, *N*-acetyl- or *N*-benzoyl-DL-leucinate), and $[CuL_2(mim)_2]\cdot 2H_2O$ (L = *N*-acetyl-α-alaninate) have been synthesized, and characterized by electronic, i.r., and e.s.r. spectroscopy. The crystal structure of the title complex has also been determined by single-crystal *X*-ray diffraction. The compound crystallizes in the triclinic space group $P\bar{1}$ with one molecule in a unit cell of dimensions a = 7.666(1), b = 8.430(1), c = 9.955(1) Å, α = 106.33(1), β = 86.27(1), and γ = 109.34(1)°. Least-squares refinement of the 215 variables gave a value of R 0.056 for 1 822 independent reflections having $F_o > 4\sigma(F_o)$. The square-planar structure consists of a copper atom lying on the centre of symmetry surrounded by two carboxylic oxygen and two *N*-methylimidazole nitrogen atoms. Electronic and e.s.r. spectroscopic data are consistent with this type of structure (CuO_2N_2 chromophore) for the hydrated complexes and with a tetragonally elongated octahedral stereochemistry (CuO_4N_2 chromophore) for the anhydrous complexes. It is suggested that the amino-acid acts as an ' asymmetric ' bidentate ligand in the latter complexes.

DURING a systematic investigation of the co-ordinative properties toward the copper(II) ion of the *N*-protected amino-acids, which, since the protecting group is an acetyl or a benzoyl group, represent the simpler systems in which one peptide linkage is present, we found that these amino-acids invariably co-ordinate through the carboxylate group.[1]

Particularly interesting are their ternary complexes with amines, since, as found in bis(*N*-acetylglycinato)-(1,10-phenanthroline)copper(II),[2] bis(hippurato)bis-(imidazole)copper(II),[3] and in bis(*N*-acetyl-DL-tryptophanato)diaquabis(pyridine)copper(II),[4] they contain heteroaromatic *N*-base moieties and *O*-donors in the co-ordination sphere of the metal. This is the preferred combination of donor atoms dominating in many naturally occurring complexes of low and high molecular weight since it enhances the complex stability.[5]

Since the presence of water molecules appears to affect the co-ordination sphere of the metal ion,[4] we have investigated the mixed-ligand complexes of copper(II) with *N*-methylimidazole (mim) and some *N*-protected amino-acids by means of spectroscopic and magnetic measurements. For one of the complexes, bis(*N*-acetyl-α-alaninato)bis(*N*-methylimidazole)copper(II) dihydrate, the crystal structure has also been determined.

EXPERIMENTAL

All chemicals were reagent grade and used as received.

Preparation of the Complexes.—All complexes were prepared by adding *N*-methylimidazole (2 × 10^{-2} mol) and diethyl ether to a methanolic or ethanolic Cu(amino-acidate)$_2\cdot x$H$_2$O (1 × 10^{-2} mol) solution.' On cooling the solution, blue compounds separated after some hours. Crystals of $[Cu(ac\text{-}\alpha\text{-}alaO)_2(mim)_2]\cdot 2H_2O$ (ac-α-ala = *N*-acetyl-α-alaninate) were obtained by slow evaporation of a methanolic solution prepared as reported above. Analytical results are given in Table 1.

Physical Measurements.—The electronic spectra of the solid compounds were recorded as mull transmission spectra with a Shimadzu MPS 50L spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 180 instrument as KBr discs or Nujol mulls on KBr discs in the range 250—4 000 cm^{-1}. The room-temperature magnetic moments were measured by the Gouy method using $[Ni(en)_3][S_2O_3]$ (en = ethylenediamine) as calibrant and correcting for diamagnetism with the appropriate Pascal constants. The room-temperature e.s.r. spectra were recorded on a JEOL PE-3X spectrometer. Quartz sample tubes were employed for polycrystalline samples. Spectra were calibrated with diphenylpicrylhydrazyl (g = 2.0036) as field marker.

TABLE 1

Analytical data

	Analysis (%) [b]		
Complex [a]	C	H	N
$[Cu(bzglyO)_2(mim)_2]\cdot H_2O$	51.9	5.15	14.2
	(51.85)	(4.95)	(13.95)
$[Cu(ac\text{-}\alpha\text{-}alaO)_2(mim)_2]\cdot 2H_2O$	41.2	6.15	16.0
	(41.25)	(6.15)	(16.05)
$[Cu(ac\text{-}\alpha\text{-}alaO)_2(mim)_2]$	44.1	6.00	17.25
	(44.3)	(5.80)	(17.25)
$[Cu(bz\text{-}\alpha\text{-}alaO)_2(mim)_2]$	54.85	5.30	13.8
	(54.9)	(5.25)	(13.75)
$[Cu(ac\text{-}\beta\text{-}alaO)_2(mim)_2]$	44.0	5.80	17.2
	(44.3)	(5.80)	(17.25)
$[Cu(bz\text{-}\beta\text{-}alaO)_2(mim)_2]$	54.9	5.25	13.65
	(54.9)	(5.25)	(13.75)
$[Cu(acleuO)_2(mim)_2]\cdot H_2O$	48.85	7.20	14.2
	(48.8)	(7.20)	(14.25)
$[Cu(bzleuO)_2(mim)_2]\cdot H_2O$	57.15	6.50	11.85
	(57.15)	(6.50)	(11.75)

[a] Abbreviations: bzglyO = benzoylglycinate; bz-α-alaO = *N*-benzoyl-α-alaninate; ac-β-alaO = *N*-acetyl-β-alaninate; bz-β-alaO = *N*-benzoyl-β-alaninate; acleuO = *N*-acetyl-DL-leucinate; bzleuO = *N*-benzoyl-DL-leucinate. [b] Calculated values are given in parentheses.

Crystal Data.—$C_{18}H_{32}CuN_6O_8$, M = 523.84, Triclinic, a = 7.666(1), b = 8.430(1), c = 9.955(1) Å, α = 106.33(1), β = 86.27(1), γ = 109.34(1)°, U = 582.2 Å^3, D_m = 1.49,

$Z = 1$, $D_c = 1.50$ g cm^{-3}, $F(000) = 275$, $\mu(\text{Cu-}K_\alpha) = 16.64$ cm^{-1}, space group $P\bar{1}$.

Cell constants were determined by diffractometry using an 'on-line' single-crystal automated Siemens AED diffractometer and refined by a least-squares procedure using the θ values of 20 high-angle reflections ($110 < 2\theta < 120°$) accurately measured at 20 °C on a crystal measuring 0.1 × 0.45 × 0.52 mm. Relative intensities were collected on the same diffractometer, by the ω—2θ scan technique using a scan speed of 2.50° min^{-1} and nickel-filtered Cu-K_α radiation ($\lambda = 1.541\ 78$ Å) operating in the range $6 < 2\theta < 120°$. The crystal was mounted with the [001] axis along the ϕ direction of the diffractometer. One reflection was measured every 50 reflections to check on alignment and the crystal and instrument stability. The individual reflection profiles were analyzed as described by Grant and Gabe.[6] The standard deviations of the intensities were evaluated from counting statistics and reflections with $F_o > 4\sigma(F_o)$ were used in the analysis. These numbered 1 822 of a possible 2 172. The structure amplitudes were obtained after the usual Lorentz and polarization corrections and transferred to an absolute scale by least squares. No correction for absorption was applied, since the μR value was very low (0.21) and, assuming a cylindrical shape for the crystal, the absorption correction coefficients are practically invariant over the range θ 3—60°.

Solution of the Structure and Refinement.—The structure was determined by the heavy-atom method. A structure-factor calculation with copper at the origin of the cell gave a conventional $R = 0.453$. Successive Fourier syntheses revealed the positions of all non-hydrogen atoms, which were refined, first isotropically, then anisotropically by several full-matrix least-squares cycles to $R = 0.079$. At this stage, the $F_o - F_c$ map was computed which revealed the positions of the hydrogen atoms. The final R, after isotropic refinement of the hydrogen atoms, was 0.056. Four reflections (100, −101, −1−13, 1−14) were excluded from the final refinement since they were affected by extinction or counting errors. The atomic scattering factors used (corrected for the anomalous dispersion of Cu) were taken from International Tables.[7] The function minimized in the least-squares calculation was $\Sigma w|\Delta F|^2$ and in the last cycles of refinement the weighting scheme $w^{-1} = \sigma^2(F_o) + 0.001(F_o)^2$ was used. All the calculations were performed using a CYBER 76 computer at the Centro di Calcolo Interuniversitario dell'Italia Nord Orientale, Bologna with the SHELX system of programs.[8] Final atomic co-ordinates are listed in Table 2. Observed and calculated structure factors and thermal parameters are available as Supplementary Publication No. SUP 23215 (14 pp.).*

Nitrogen, carbon, and hydrogen were analyzed by Mr. G. Pistoni using a Carlo Erba elemental analyzer model 1106.

TABLE 2

Atomic fractional co-ordinates (× 10^4 for Cu, O, N, and C; × 10^3 for H) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cu	0	0	0
O(1)	1 814(5)	768(4)	1 521(3)
O(2)	−318(4)	−666(5)	2 732(4)
O(3)	3 436(5)	−2 350(5)	3 376(4)
O(4)	3 896(6)	1 288(6)	−1 501(5)
N(1)	2 266(5)	−306(5)	4 681(4)
N(2)	−594(6)	2 171(5)	704(5)
N(3)	−2 222(6)	3 938(5)	1 224(4)
C(1)	1 250(5)	219(5)	2 580(5)
C(2)	2 714(6)	793(6)	3 735(5)
C(3)	2 973(8)	2 667(6)	4 560(6)
C(4)	2 666(6)	−1 790(6)	4 436(5)
C(5)	2 111(9)	−2 745(7)	5 533(7)
C(6)	−2 213(7)	2 300(6)	594(5)
C(7)	−3 810(16)	4 519(16)	1 341(15)
C(8)	−506(7)	4 896(6)	1 745(6)
C(9)	509(8)	3 807(6)	1 436(5)
H(1)	388(6)	59(6)	320(5)
H(2)	332(8)	324(8)	368(7)
H(3)	400(8)	313(8)	528(6)
H(4)	176(8)	274(7)	495(7)
H(5)	165(7)	0(7)	551(6)
H(6)	99(9)	−355(8)	530(7)
H(7)	309(9)	−329(8)	568(7)
H(8)	189(9)	−182(9)	648(8)
H(9)	−329(7)	143(7)	38(6)
H(10)	−472(10)	380(10)	102(8)
H(11)	−386(10)	505(11)	227(10)
H(12)	−351(10)	550(10)	78(10)
H(13)	−11(7)	600(7)	228(6)
H(14)	183(8)	401(7)	159(6)
H(15)	291(11)	124(9)	−154(8)
H(16)	469(10)	156(9)	−215(8)

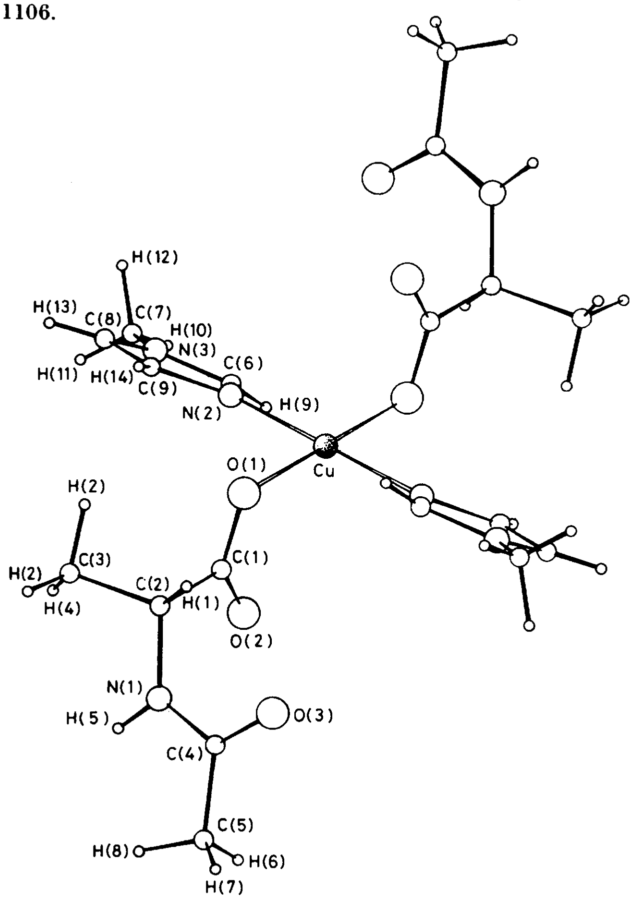

FIGURE 1 Perspective view of the structure

RESULTS AND DISCUSSION

Description of the Structure of Bis(N-*acetyl-α-alaninato*)-*bis*(N-*methylimidazole*)*copper*(II) *Dihydrate.*—A projection of the structure showing the numbering of the atoms is given in Figure 1. The complex is monomeric and

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

square planar, with the copper atom lying on the symmetry centre surrounded by two carboxylic oxygen and two imidazole nitrogen atoms. The peptide group is not involved in the co-ordination and Cu–O(2) (carboxylic) and Cu–O(4) (water) distances are 2.907(4) and 3.241(4) Å respectively. The final interatomic distances and angles are given in Table 3.

TABLE 3

Bond distances (Å) and angles (°) with estimated standard deviations in parentheses

Cu–O(1)	1.942(3)	C(4)–C(5)	1.493(9)
Cu–N(2)	1.959(5)	C(4)–O(3)	1.228(6)
O(1)–C(1)	1.263(6)	N(2)–C(6)	1.295(8)
O(2)–C(1)	1.212(5)	N(3)–C(6)	1.349(6)
C(1)–C(2)	1.520(6)	N(3)–C(7)	1.442(15)
C(2)–C(3)	1.514(6)	N(3)–C(8)	1.342(6)
C(2)–N(1)	1.450(7)	C(8)–C(9)	1.351(9)
N(1)–C(4)	1.338(7)	N(2)–C(9)	1.375(5)
C(2)–H(1)	1.05(5)	C(7)–H(10)	0.77(6)
C(3)–H(2)	1.09(8)	C(7)–H(11)	0.91(9)
C(3)–H(3)	1.00(6)	C(7)–H(12)	1.08(10)
C(3)–H(4)	1.00(6)	C(8)–H(13)	0.89(5)
C(5)–H(6)	0.90(6)	C(9)–H(14)	0.98(6)
C(5)–H(7)	1.04(8)	O(4)–H(15)	0.75(9)
C(5)–H(8)	1.09(7)	O(4)–H(16)	0.88(8)
C(6)–H(9)	0.89(4)	N(1)–H(5)	0.94(5)
O(1)–Cu–N(2)	90.3(2)	O(1)–C(1)–C(2)	114.5(4)
Cu–O(1)–C(1)	115.6(3)	N(1)–C(2)–C(1)	113.1(4)
C(2)–N(1)–C(4)	123.4(4)	C(1)–C(2)–C(3)	109.4(4)
Cu–N(2)–C(9)	129.6(4)	N(1)–C(2)–C(3)	109.4(4)
Cu–N(2)–C(6)	124.5(4)	O(3)–C(4)–N(1)	122.7(5)
C(6)–N(2)–C(9)	105.9(4)	N(1)–C(4)–C(5)	115.9(5)
C(7)–N(3)–C(8)	126.9(6)	O(3)–C(4)–C(5)	121.4(5)
C(6)–N(3)–C(8)	107.4(5)	N(2)–C(6)–N(3)	111.2(5)
C(6)–N(3)–C(7)	125.7(6)	N(3)–C(8)–C(9)	106.6(5)
O(1)–C(1)–O(2)	125.4(4)	N(2)–C(9)–C(8)	109.0(5)
O(2)–C(1)–C(2)	120.1(4)		

The copper(II)–carboxylate oxygen bond is similar to those found in other copper(II) carboxylate complexes [9,10] and the Cu–N(2) distance is very close to the Cu–N bond length of 1.953(5) Å found in *catena*-di-μ-bromo-bis(*N*-methylimidazole)copper(II) [11] and 1.962(4) and 1.975(5) Å found in *trans*-dichlorobis(*N*-methylimidazole)-copper(II).[12]

Bond distances and angles in the *N*-acetyl-α-alaninate moiety and in the *N*-methylimidazole molecule are in good agreement with those of L-alanine,[13] of other *N*-substituted α-amino-acids,[14,15] and of copper–amino-acid and -imidazole complexes.[9-12]

Equations of the best planes and the displacements of atoms from these planes are listed in Table 4. The C^{α}–COO group is planar with the amino-nitrogen 0.48 Å out of this plane. The *N*-methylimidazole molecule forms an angle of 85° with the carboxylate plane and 83° with the plane through the peptide groups. The dihedral angle between carboxylate and peptide groups is 86°.

The conformation of the *N*-acetyl-α-alaninate residue can be described using the torsion angles defined by the IUPAC–IUB Commission of Biochemical Nomenclature (1970): $\omega = 179.6^\circ$, $\phi = 85.5^\circ$, $\psi = -159.4^\circ$, O(3) lying *cis* and C(5) *trans* to the N(1)–C(2) bond. This conformation is a consequence of the steric hindrance due to the water molecules in the cell. As shown in Figure 2 and in Table 5, the water molecule extends the structure in all directions, forming strong hydrogen bonds with peptidic and unco-ordinated carboxylic oxygen atoms. The unco-ordinated carboxylic oxygen atom also forms a hydrogen bond with an adjacent peptidic nitrogen atom.

TABLE 4

Least-squares planes.* Deviations (Å) from the planes are given in square brackets

Plane 1: Carboxyl group

$$0.530\,70X - 0.740\,03Y - 0.413\,08Z = -0.066\,22$$

[O(1) − 0.002, C(1) 0.007, O(2) − 0.002, C(2) − 0.002, *N*(1) 0.476]

Plane 2: Peptide group

$$-0.788\,82X - 0.396\,82Y - 0.469\,36Z = -3.1714$$

[N(1) 0.003, C(4) − 0.001, O(3) 0.001, C(5) − 0.003, C(2) − 0.003, *C*(1) 1.387, *C*(3) − 0.661]

Plane 3: Methylimidazole molecule

$$0.119\,09X - 0.496\,76Y - 0.859\,68Z = 0.063\,55$$

[N(2) − 0.001, C(6) 0.003, N(3) − 0.003, C(8) 0.006, C(9) − 0.002, *C*(7) − 0.049]

* Equations of the planes are given in the form $AX + BY + CZ = D$ with respect to an orthogonal system where X, Y, Z, and D are in Å. Italicized atoms are not included in the plane.

Spectroscopic and Magnetic Results.—The room-temperature electronic spectra (Table 6) of all the complexes in the solid state are similar in band shape and positions, consistent with the presence of tetragonally elongated ligand fields. In particular, the high ligand fields observed for all the complexes, except the β-alaninate and benzoyl-leucinate derivatives, in agreement with the structural data for $[Cu(ac\text{-}\alpha\text{-}alaO)_2(mim)_2]\cdot 2H_2O$, are due to the fact that the amino-acid acts as a unidentate ligand bonding through only one oxygen atom of the carboxylate group. This gives rise to an essentially square-planar environment around the copper(II) ion.

TABLE 5

Hydrogen bonds (Å) and angles (°) subtended by them *

O(4) · · · O(2^{I})	2.902(6)	O(2^{I}) · · · H(15)–O(4)	152
O(2^{I}) · · · H(15)	2.22		
O(4)–H(15)	0.75		
O(4) · · · O(3^{II})	2.775(6)	O(3^{II}) · · · H(16)–O(4)	173
O(3^{II}) · · · H(16)	1.90		
O(4)–H(16)	0.88		
N(1) · · · O(2^{III})	2.942(5)	O(2^{III}) · · · H(5)–N(1)	17
O(2^{III}) · · · H(5)	2.00		
N(1)–H(5)	0.94		

* Roman numeral superscripts refer to the symmetry transformations: I $\bar{x},\bar{y},\bar{z}$; II $1 - x,\bar{y},\bar{z}$; III $\bar{x},\bar{y},1 - z$.

In the acetyl- and benzoyl-β-alaninate complexes the spectral changes may be explained by the axial approach of additional O atoms. The spectroscopic results agree with those reported for bis(benzoylglycinato)bis(imidazole)copper(II), in which the amino-acid is found to act

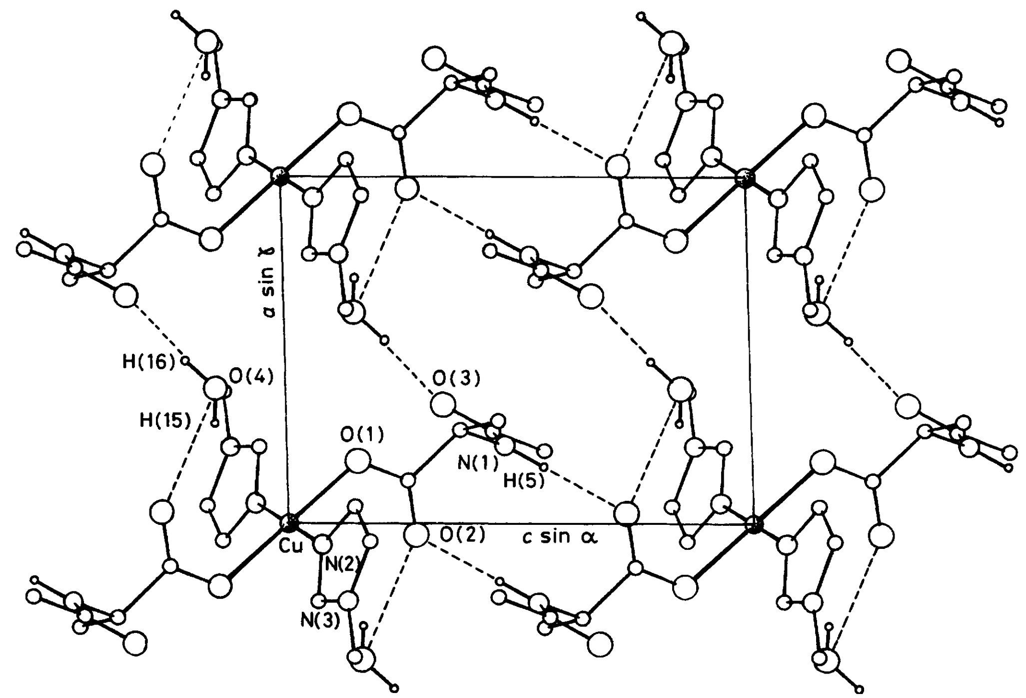

FIGURE 2 Projection of the structure along the [010] axis

as an 'asymmetric' bidentate ligand bonding through the oxygens of the carboxylate group [Cu–O(1) 1.976(3) and Cu–O(2) 2.736(4) Å],[3] and for other complexes having a CuO_4N_2 chromophore.[4,16-18]

All the solid complexes show a 'normal' room-temperature magnetic moment for an orbitally non-degenerate ground state. Polycrystalline e.s.r. spectra (Table 6) of axial type suggest an essentially $d_{x^2-y^2}$ ground state, with experimental g values in the range expected for tetragonally elongated octahedral complexes in which mixed *O*- and *N*-donor groups are present.[18-20]

TABLE 6

Room-temperature spectroscopic and magnetic properties of the solid complexes [a]

Complex	d–d Bands/ 10^3 cm^{-1}	$\tilde{\nu}_{asym}$(OCO)/ cm^{-1}	$\tilde{\nu}_{sym}$(OCO)/ cm^{-1}	$\Delta\nu$	$\mu_{eff.}$ [b]/ B.M.	$g_{\parallel}$	$g_{\perp}$	$\langle g\rangle$ [c]	$A_{\parallel}$/ 10^{-4} cm^{-1}
$[Cu(bzglyO)_2(mim)_2]\cdot H_2O$ [d]	15.4 (sh), 18.2	1 598vs	1 382s	216	1.80	2.201	2.048	2.099	
$[Cu(ac\text{-}\alpha\text{-}alaO)_2(mim)_2]\cdot 2H_2O$ [d]	15.4 (sh), 18.2	1 609vs	1 403vs	206	1.82	2.243	2.040	2.108	188
$[Cu(ac\text{-}\alpha\text{-}alaO)_2(mim)_2]$	14.9 (sh), 18.0	1 596vs	1 396vs	200	1.87	2.227	2.049	2.108	177
$[Cu(bz\text{-}\alpha\text{-}alaO)_2(mim)_2]$	15.3 (sh), 18.1	1 612vs	1 388vs	224	1.91	2.212	2.053	2.106	
$[Cu(ac\text{-}\beta\text{-}alaO)_2(mim)_2]$	14.8 (sh), 16.8	1 600vs	1 392vs	208	1.93	2.261	2.047	2.118	148
$[Cu(bz\text{-}\beta\text{-}alaO)_2(mim)_2]$	14.8 (sh), 17.4	1 598vs	1 392vs	206	1.94	2.261	2.053	2.122	158
$[Cu(acleuO)_2(mim)_2]\cdot H_2O$ [d]	15.3 (sh), 18.2	1 610vs	1 385vs	225	1.88	2.273	2.047	2.136	184
$[Cu(bzleuO)_2(mim)_2]\cdot H_2O$ [d]	15.7	1 618vs	1 380vs	238	1.94	2.212	2.075	2.121	

[a] For ligand abbreviations see footnote *a*, Table 1. [b] 1 B.M. = 9.274×10^{-24} A m^2. [c] $\langle g\rangle = \frac{1}{3}(g_{\parallel} + 2g_{\perp})$. [d] Bands around 3 440 and 3 520 cm^{-1} assignable to ν_{sym}(OH) and ν_{asym}(OH) respectively, of the water molecules are observed.

For the structurally characterized $[Cu(ac\text{-}\alpha\text{-}alaO)_2(mim)_2]\cdot 2H_2O$ complex, which contains only one molecule in the unit cell, the crystal g values are also molecular g values. The $A_{\parallel}$ values for the β-alaninate complexes are lower than those of the other complexes, confirming that there is less tetragonal distortion in the former than in the latter.[18,21]

It is difficult to assign the different types of carboxylate co-ordination on the basis of the number of i.r.- or Raman-active vibrations due to the low symmetry of carboxylate ions.[22] There are also numerous factors which may affect the positions and separations of the carbon–oxygen stretching frequencies.[23-25] Although back bonding from the metal ion to the aromatic amine (which stabilizes the ternary complex) may also affect the carboxylate stretching frequencies, it is possible to suggest that the ligand bonds in a unidentate manner through the carboxylic group by comparing the more relevant bands of the i.r. spectra of the complexes with those of the structurally known compound (Table 6).[4]

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