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(N-acetyl-DL-valinate)copper(II) Complexes: Effect of Amines on the Amino-acid Co-ordination

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Two compounds, $Cu(AcVal)_2$ and $Cu(AcVal)_2 \cdot H_2O$, and their amine adducts, $Cu(AcVal)_2B_n$ (AcVal = N-acetyl-DL-valinate ion; n = 1 and B = 1,10-phenanthroline, 2,2'-bipyridyl and piperazine; n = 2 and B = pyridine, 3- and 4-methylpyridine, pyridazine, N-methylpiperazine, morpholine and piperidine) were prepared and investigated by means of room temperature infrared, electronic and e.p.r. spectroscopy and low and room temperature magnetic susceptibilities. The results suggest a tetragonal configuration for the $Cu(AcVal)_2$, with CuO_4 chromophore, and for the amine adducts, with essentially CuO_2N_2 chromophore, and a binuclear configuration for the $Cu(AcVal)_2 \cdot H_2O$, which shows an exchange integral $(-2J)$ of 351 ± 9 cm^{-1} and a zero field splitting D of 0.39 cm^{-1} which are in the range found for the copper acetate monohydrate complex and other similar complexes. The amino acid coordinates by the carboxylate group in all the complexes.

Introduction

The donor properties of amino acids and peptides as models for metal–protein interaction have interested the coordination chemist for many years. In particular, molecules that contain only one peptide linkage offer the simplest systems in which the effect of various structural features of a protein-like donor molecule on the mode of coordination about the metal ion may be investigated [1].

Being interested in this field (see for example ref. [2–5]), in this paper we have investigated the coordination properties of the N-acetyl-DL-valine (hereafter abbreviated as AcValH) with the copper(II) ion and the effect of additional ligands, such as aliphatic and aromatic heterocyclic amines, on the amino acid coordination.

Experimental

Preparation of the Complexes

$Cu(AcVal)_2$ complex was prepared by adding a copper(II) perchlorate hexahydrate (1 mmol) solution in anhydrous ethanol to a N-acetyl-DL-valine (2 mmol) solution, neutralized with a stoichiometric amount of potassium hydroxide, in anhydrous ethanol. The potassium perchlorate precipitated was filtered off and the solution cooled at 4–5 °C for some hours; blue crystals separated. $Cu(AcVal)_2 \cdot H_2O$ was obtained by recrystallization of the $Cu(AcVal)_2$ complex in water.

$Cu(AcVal)_2B_n$ (n = 1 and B = ophen; n = 2 and B = py, 3pic, 4pic, Mepipz and pipd) complexes precipitated after some days by cooling a $Cu(AcVal)_2 \cdot H_2O$ ethanolic solution containing an amine excess.

$Cu(AcVal)_2B_n$ (n = 1 and B = bipy, pipz; n = 2 and B = pid, morph) complexes were obtained by cooling a $Cu(AcVal)_2 \cdot H_2O$ methanolic solution containing an amine excess.

Physical Measurements

The i.r. spectra of the solid compounds in KBr or nujol were recorded with a Perkin Elmer 180 spectrophotometer in the 4000–250 cm^{-1} spectral range. The room-temperature electronic spectra of the solid compounds were recorded as mull transmission spectra with a Shimadzu MPS 50L spectrophotometer. The low and room temperature magnetic moments were measured with the Gouy method, using $Nien_3S_2O_3$ as calibrant and correcting for diamagnetism with the appropriate Pascal constants. The e.p.r. spectra were recorded on a JEOL PE-3X spectrometer; quartz sample tubes were employed for polycrystalline samples. Spectra were calibrated with diphenylpicrylhydrazyl (DPPH, g = 2.0036) as a field marker.

Analyses

Nitrogen, carbon and hydrogen were determined with a Perkin Elmer 240 Elemental Analyser by Mr. G. Pistoni.

Results and Discussion

The prepared compounds, their analyses and the abbreviated names of the amino acid and the amines

TABLE I. Conventional Chemical Analyses.[a]

		C %		H %		N %	
		calcd	found	calcd	found	calcd	found
$Cu(AcVal)_2$	blue	44.24	44.14	6.38	6.25	7.38	7.16
$Cu(AcVal)_2 \cdot H_2O$	green	42.24	42.75	6.59	6.67	7.04	6.99
$Cu(AcVal)_2(py)_2$	blue	51.38	51.18	6.67	6.86	10.90	10.05
$Cu(AcVal)_2(3pic)_2$	blue	55.31	55.42	6.77	6.84	9.90	9.83
$Cu(AcVal)_2(4pic)_2$	blue	55.31	55.30	6.77	7.01	9.90	10.25
$Cu(AcVal)_2(pid)_2$	blue	48.90	48.72	5.97	6.16	15.57	15.56
$Cu(AcVal)_2 \cdot ophen \cdot 2H_2O$	blue	52.36	52.12	6.09	6.15	9.40	9.44
$Cu(AcVal)_2 \cdot bipy$	blue	53.75	53.60	6.02	6.08	10.46	10.49
$Cu(AcVal)_2 \cdot pipz \cdot 2H_2O$	blue	43.04	43.54	7.63	7.60	11.16	11.28
$Cu(AcVal)_2(Mepipz)_2$	blue	49.66	50.58	8.34	8.25	14.49	14.49
$Cu(AcVal)_2(morph)_2$	blue	47.66	47.75	7.64	7.70	10.11	10.10
$Cu(AcVal)_2(pipd)_2$	lilac	52.37	52.46	8.43	8.67	10.19	10.34

[a]Abbreviations: AcVal = N-acetyl-DL-valinate ion; py = pyridine; 3- or 4-pic = 3- or 4-methylpyridine; pid = pyridazine; bipy = 2,2'-bipyridyl; ophen = 1,10-phenanthroline; pipz = piperazine; Mepipz = N-methylpiperazine; morph = morpholine; pipd = piperidine.

TABLE II. Room Temperature Electronic and E.p.r. Spectra, and Magnetic Moments for the Solid Complexes.

	d–d Bands kK			μ_{eff} B.M.	$g_\parallel$	$g_\perp$	g_0		
$Cu(AcVal)_2$	13.0	16.9		1.80	2.304	2.066	2.145		
$Cu(AcVal)_2(py)_2$	13.6sh	16.4		1.78	2.322	2.074	2.157		
$Cu(AcVal)_2(3pic)_2$	12.5sh	15.2		1.84	2.272	2.066	2.135		
$Cu(AcVal)_2(4pic)_2$	13.5sh	16.7		1.81	2.234	2.073	2.127		
$Cu(AcVal)_2(pid)_2$	12.5sh	15.1	26.0sh	1.88	2.241	2.079	2.133		
$Cu(AcVal)_2 \cdot ophen \cdot 2H_2O$	12.2sh	14.7		1.86	2.179	2.074	2.109		
$Cu(AcVal)_2 \cdot bipy$	14.3sh	17.2	24.4sh	1.87	2.253	2.063	2.126		
$Cu(AcVal)_2 \cdot pipz \cdot 2H_2O$	14.1sh	17.0		1.79	2.249	2.054	2.119		
$Cu(AcVal)_2(Mepipz)_2$	13.3sh	16.0		1.88	2.331	2.075	2.160		
$Cu(AcVal)_2(morph)_2$	13.3sh	15.6		1.87	2.243	2.077	2.132		
$Cu(AcVal)_2(pipd)_2$	15.4sh	19.1		1.85	2.272	2.074	2.140		
					Monomer		Dimer		D cm^{-1}
					$g_\parallel$	$g_\perp$	g_z	$g_\perp$	
$Cu(AcVal)_2 \cdot H_2O$	13.9		26.3sh	1.34	2.197	2.047	2.397	2.106	0.39

[a]$\lambda = -825$ cm^{-1}.

are reported in Table I. All the complexes are stable in air and soluble in polar organic solvents, while the aromatic heterocyclic amine adducts are also soluble in chloroform.

The copper(II)–amino acid interaction gives rise to the formation of two complexes, the blue anhydrous and the green monohydrate bis(N-acetyl-DL-valinate)copper(II), which show different physical properties.

The room temperature e.p.r. spectrum of the anhydrous bis(N-acetyl-DL-valinate)copper(II) complex ($Cu(AcVal)_2$) in the solid state is a typical axial spectrum with two g values (Table II and Fig. 1), which indicates a predominantly $d_{x^2-y^2}$ ground state and an essentially square planar arrangement around the copper(II) ion [6–8]. In particular, the g crystal values are typical of compounds having a CuO_4 chromophore [9, 10] and the broad e.p.r. line excludes the presence of exchange effects between neighbouring copper(II) ions [8], as is also confirmed by its 'normal' room temperature magnetic moment. Its room temperature electronic spectrum (Table II and Fig. 2) shows two well resolved sharp bands at 12990 and 16890 cm^{-1}, which strongly resemble those

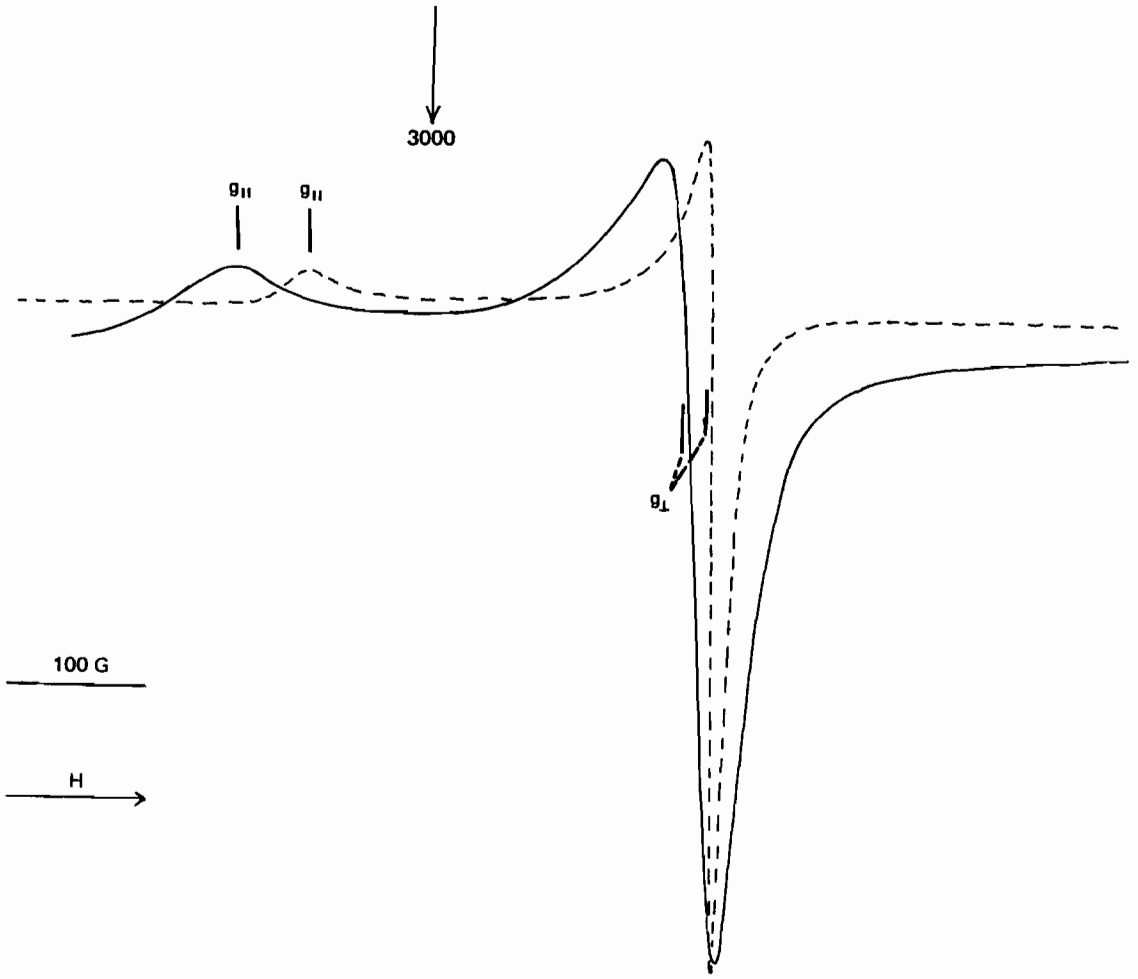

Fig. 1. Room temperature e.p.r. spectra of the $Cu(AcVal)_2$ (——) and $Cu(AcVal)_2 \cdot pipz \cdot 2H_2O$ (····) complexes in the solid state.

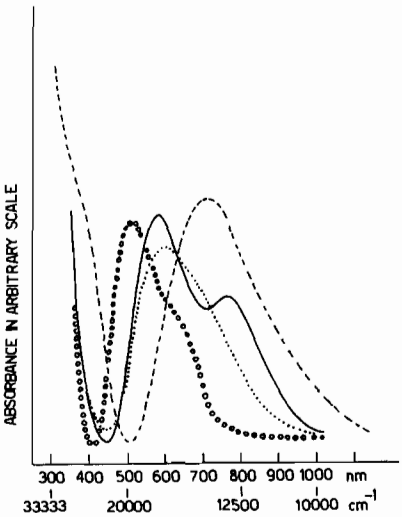

Fig. 2. Exemplifying room temperature solid electronic spectra of the $Cu(AcVal)_2$ (——), $Cu(AcVal)_2 \cdot H_2O$ (– – –), $Cu(AcVal)_2(py)_2$ (····) and $Cu(AcVal)_2(pipd)_2$ (○○○○) complexes.

reported for tetragonal copper(II)–oxygen systems [10]. In fact cubic octahedrally coordinated copper(II), having ^2E_g ground state, shows one excited state, $^2T_{2g}$, which splits under tetragonal distortion so that as many as three d–d transitions may become possible [11].

The green bis(N-acetyl-DL-valinate)copper(II) monohydrate ($Cu(AcVal)_2 \cdot H_2O$) complex displays magnetic and spectral characteristics similar to those reported for copper(II) acetate monohydrate and similar binuclear species [12–17], for which the presence of analogous binuclear entities may be suggested. The corrected molar susceptibility and magnetic moment (Table III) of this complex indicate the presence of strongly coupled pair of copper(II) ions. The corrected molar susceptibility varies with temperature (Fig. 3), but no maximum in the curve is found in the temperature range studied. However the experimental data can also be fitted closely by the Bleaney–Bowers Equation [18], so that, following the procedure adopted by Martin *et al.* [19] a $-2J$ value of 351 ± 9 cm^{-1} may be calculated at different tempe-

TABLE III. Experimental and Calculated Corrected Molar Susceptibilities and Magnetic Moments for the Bis(N-acetyl-DL-valinate)copper(II) Monohydrate Complex.

Temp. K	Experimental		Calculated	
	$10^6\chi_M$	μ_{eff}	$10^6\chi_M$	μ_{eff}
101	194	0.40	179	0.38
127	293	0.55	314	0.57
155	467	0.76	465	0.76
174	604	0.92	554	0.88
202	674	1.04	654	1.03
231	712	1.15	726	1.16
250	750	1.23	753	1.23
275			776	1.31
293	765	1.34	787	1.36
320			789	1.42
350			783	1.48
375			773	1.52
400			761	1.56

ratures. The parameters used are g = 2.21, as experimentally found from the e.p.r. spectrum, and Nα fixed at 60 × 10^{-6} c.g.s. units. The −2J value falls in the range expected for dimeric copper(II) carboxylates [17]. From the calculated curve, with the parameters −2J = 351 cm^{-1}, g = 2.21 and Nα = 60 × 10^{-6} c.g.s. units, a maximum in susceptibility at about 320 K is recognized (Fig. 3).

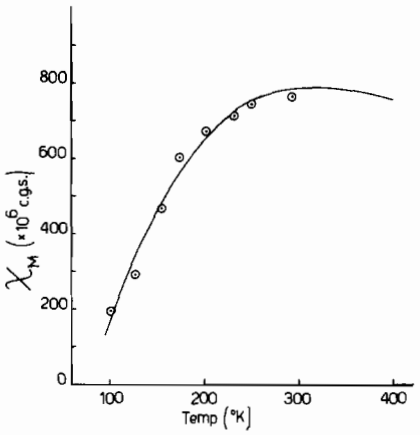

Fig. 3. Variation of magnetic susceptibility with temperature of the $Cu(AcVal)_2 \cdot H_2O$ complex. ⊙ experimental susceptibility, dashed line calculated.

The e.p.r. spectrum of the green monohydrate complex (Fig. 4), characteristic of binuclear species [17], shows zero field splitting of 0.39 cm^{-1} and the presence of magnetically dilute copper(II) impurities.

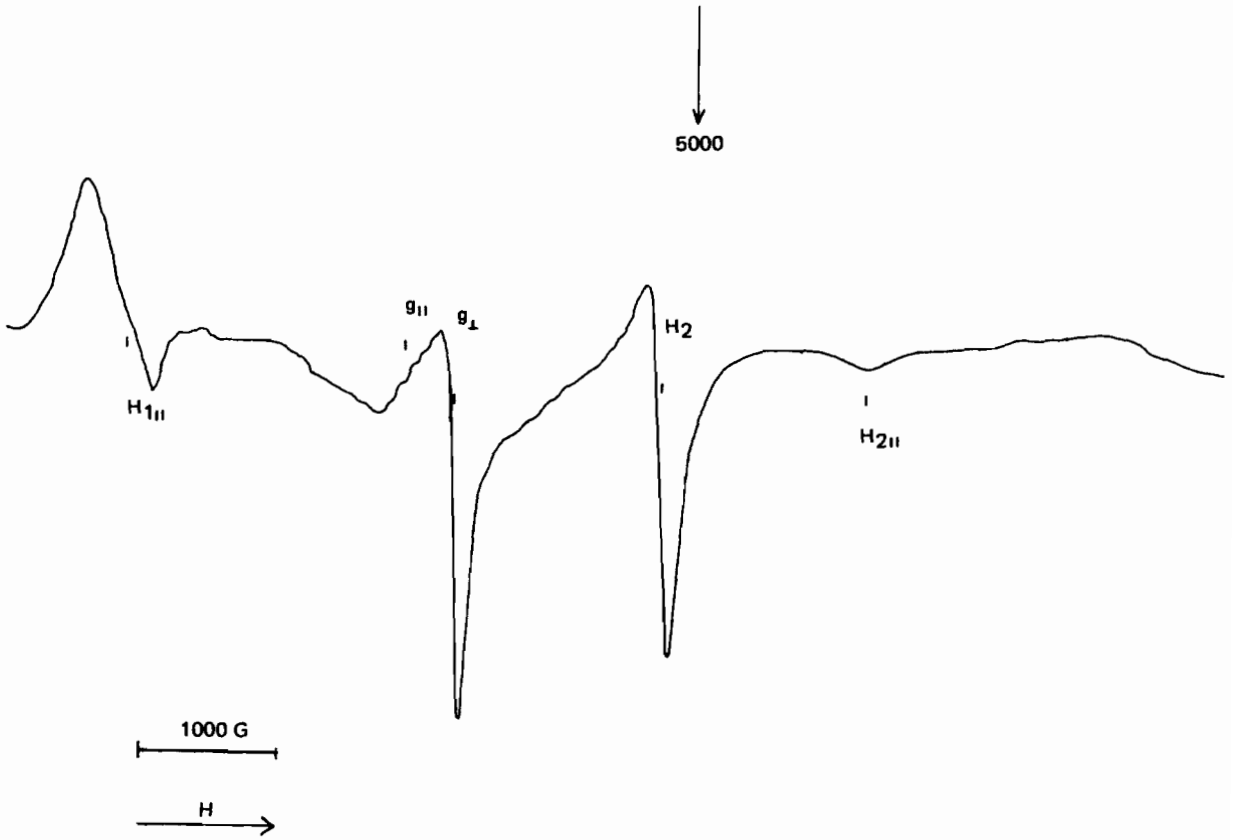

Fig. 4. Room temperature e.p.r. spectrum of the $Cu(AcVal)_2 \cdot H_2O$ complex in the solid state.

Its electronic spectrum (Fig. 2) also agrees with the presence of binuclear species; in particular, a band is present at 26320 cm^{-1} which is considered peculiar to these type of compounds [14, 16, 20].

All the amine adducts, which have 'normal' room temperature magnetic moments, show room temperature electronic spectra with a band envelope centered at 14000–19000 cm^{-1} (Table II and Fig. 2), indicating tetragonally distorted ligand fields consistent with the presence of an essentially CuO_2N_2 chromophore. The shift of the d–d bands to higher energies in the order pipd > pipz > 4pic > py > Mepipz > morph > 3pic > pid indicates an increase of the tetragonal distortion in the same order.

The e.p.r. results obtained on polycrystalline samples are summarized in Table II. For all the adducts the e.p.r. line shapes are quite similar to each other, all the spectra being of axial type. In particular, the values found for the parallel components of the g and A (only for three complexes) tensors, in agreement with the electronic results, indicate the presence of tetragonal elongated structures. g values, lower than those found for the anhydrous and monohydrate bis(N-acetyl-DL-valinate)copper(II) complexes and for other complexes, having CuO_4 chromophore [9, 10], suggest the presence of essentially CuO_2N_2 chromophore in all the amine adducts as a consequence of the amine coordination [10, 21].

For the $Cu(AcVal)_2 \cdot pipz \cdot 2H_2O$ complex the narrow e.p.r. line (Fig. 1) ($\Delta H_{\parallel}$ = 20 G; $\Delta H_{\perp}$ = 6 G) is observed. This may be strongly indicative of the presence of exchange interactions due to the piperazine molecules 'bridging' two copper(II) ions [8, 22].

The coordination sites of the amino acid may be identified, as the i.r. spectra of all the complexes are very similar in shape and position of the bands to those of the sodium and potassium N-acetyl-DL-valinate salts and of the monohydrate bis(N-acetyl-DL-valinate)copper(II) complex, for which the electronic and e.p.r. results are straightforward in the assignment of the amino acid coordination. On this basis we may conclude that the carboxylate group is the only ligand site involved in the coordination of the copper(II) ion in all the complexes reported in this work, confirming the suggestion deduced from the electronic and e.p.r. spectra. This, moreover agrees with our previous studies on the interactions of the transition metal ions with simple N-protected amino acids, containing a peptide group. In fact we have found that N-acetyl- and N-benzoyl-glycine, N-acetyl-L-, α-N-benzoyl-DL and N-benzoyl-β-alanine and N-acetyl-DL-leucine coordinate the metal ions only toward the carboxylate group [2–5, 23]. This is also consistent with simple ligand field considerations, as the introduction of a substituent, directly on the amino group, reduces the ligand field of the in-plane donor diminishing the affinity of the amino group for the metal ion.

Steric considerations also confirm our conclusions, for it is known that the peptidic nitrogen atom links a metal only when the process is accompanied by the dissociation of the peptide proton, as the peptide group does not lose the peptide group resonance, and the metal–N(peptide) bond exists in common with two adjacent chelate rings [24].

Trends in positions of and separation ($\Delta\nu$) between antisymmetric and symmetric carboxylate stretching bands provide a useful observation for

TABLE IV. More Relevant I.r. Bands (cm^{-1}) of the Solid Complexes.

	ν(NH)	$\nu(CO)_{ket}$	$\nu(OCO)_{as}$	$\nu(OCO)_s$	$\Delta\nu$
AcValH	3364s	1592vs	1710vs	1212vs	498
AcValNa	3298s	1655vs	1588vs	1407s	181
AcValK	3280ms	1640vs	1587vs	1394vs	193
$Cu(AcVal)_2 \cdot H_2O$[a]	3305ms	1650sh	1610vs	1410vs	200
$Cu(AcVal)_2$	3260ms	1640s	1575vs	1375s	200
$Cu(AcVal)_2(py)_2$	3318, 3260ms	1670s	1590vs	1388vs	202
$Cu(AcVal)_2(3pic)_2$	3313ms	1662s	1588vs	1385vs	203
$Cu(AcVal)_2(4pic)_2$	3308, 3250s	1660s	1588vs	1378vs	210
$Cu(AcVal)_2(pid)_2$	3318s	1660vs	1585s	1402s	183
$Cu(AcVal)_2 \cdot ophen \cdot 2H_2O$	3290s	1655sh	1583vs	1386vs	197
$Cu(AcVal)_2 \cdot bipy$	3332s	1658s	1582vs	1402vs	180
$Cu(AcVal)_2 \cdot pipz \cdot 2H_2O$	3270s (3180w)[b]	1640sh	1610vs	1370vs	240
$Cu(AcVal)_2(Mepipz)_2$	3318s (3158m)[b]	1638sb	1580vs	1392vs	188
$Cu(AcVal)_2(morph)_2$	3318s (3150m)[b]	1640vs	1573vs	1395vs	178
$Cu(AcVal)_2(pipd)_2$	3285m (3170m)[b]	1652s	1588vs	1392s	196

[a]For this complex two bands, assignable to the coordinated water molecules, appear at 3500sh, 3425ms cm^{-1}. [b]ν(NH) of the aliphatic heterocyclic amines.

assigning the coordination type of the carboxylate group. In fact a unidentate coordination, as the CO bonds become inequivalent, may be expected to show a large splitting of the carboxylate stretching frequencies, while an asymmetric, symmetric or bridging bidentate coordination must present a small splitting [17, 25–27]. This is only true in the absence of any strong hydrogen bonding effects, which involve the amino acid [26, 27]. The $\Delta\nu$ separation found in the 183–210 cm^{-1} range in all the complexes, except the pipz adduct, suggests a bidentate coordination, which may be generally asymmetric of the type previously found in the structurally known N-acetylglycinate-copper(II) complexes [3, 4].

In the monohydrate bis(N-acetyl-DL-valinate)-copper(II) complex a high energy shift of the antisymmetric and symmetric carboxylate stretching frequencies further confirms the presence of a carboxylate group, bridging two copper(II) ions [13, 14, 25–27].

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