Cobalt(II), Nickel(II) and Zinc(II) Complexes of Peptide-Group Containing Amino Acids. Bis(N-Acetyl-DL-Valinate)Metal(II) Complexes and their Amine Adducts

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First row transition metal(II) complexes of N-acetyl-DL-valine of the type $M(AcVal)_2 \cdot xH_2O$ (M = Co(II), Ni(II) and x = 2; M = Zn(II) and X = 0) and their amine adducts of the type $M(AcVal)_2B_2 \cdot xH_2O$ (M = Co(II), Ni(II) and Zn(II); B = pyridine, 3- and 4-methylpyridine, 1,10-phenanthroline) were prepared and investigated by means of magnetic measurements, electronic, infrared and ^1H n.m.r. spectroscopy. Magnetic moments and electronic spectra of the Co(II) and Ni(II) compounds, consistent with hexacoordinated metal(II) with some distortion from the O_h symmetry, suggest the presence of MO_6 and MO_4N_2 chromophores for the hydrate and base adducts, respectively. By comparing the Dq values of the present complexes and those of the other N-substituted amino acids previously studied, a spectrochemical series of the amino acid ligands is constructed. Also the infrared spectra agree with the coordination of the amino acid toward the carboxyl group. The trans-effect of the amines, with respect to that of the water, results in a weakening of the N-acetyl-DL-valinate coordination strength in the order py > 4pic > 3pic, as steric effects prevail over the inductive effects. The solution electronic and infrared spectra, which are very similar to those of the solid compounds, and the ^1H n.m.r. spectra of the diamagnetic zinc(II) complexes indicate that the same complexes also exist in solution. The coupling of the CHNH group in the ^1H n.m.r. spectra and the shift of the ν(NH) and δ(NH) vibrations in the infrared spectra of the solution, with respect to the solid complexes, indicate that the hydrogen bonding of the NH group present in the solid complexes is removed in chloroform solution.
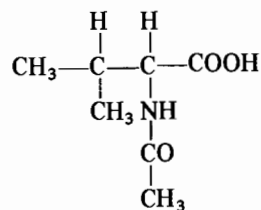
Introduction

First row transition metal(II) complexes of amino acids have been investigated in considerable detail and if there are no complicating donor side chains the acids coordinate solely through the amino- and carboxylato-groups, forming stable five- or six-membered chelate rings with the metal ion.

In the peptide complexes the N(peptide) atom binds a metal only when the process is accompanied by the dissociation of the peptide proton and the formation of metal–N(peptide) bonds are limited to the d^6–d^9 first row transition metals [1].

A third type of coordination was evidentiated in the metal complexes of simple amino acids containing a peptide group, as N-acetyl-, N-benzoyl-glycine, benzoyl-β-, α-N-benzoyl-DL- and N-acetyl-L-alanine in which the coordination occurs toward the carboxylato group [2–4], while the peptide-group is only involved in hydrogen bonding interactions in the crystal packing [5, 6].

In this paper we have now considered the coordination properties of the N-acetyl-DL-valine (AcValH):

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{\underset{\underset{\underset{CH_3}{|}}{CO}}{|}}{NH}}{\overset{\overset{H}{|}}{C}}-COOH$$

with metal ions which may favour the peptide group coordination like Co(II) and Ni(II), or not, like Zn(II). The effect of additional ligands, such as aromatic heterocyclic amines, on the amino acid coordination is also examined.

Experimental

Preparation of the complexes

$M(AcVal)_2 \cdot xH_2O$ (M = Co, Ni and x = 2; M = Zn and x = 0) complexes were obtained by adding a

TABLE I. Analyses and Magnetic Moments of the Solid Complexes.[a]

		C%		H%		N%		μ_{eff} B.M.
		calcd.	found	calcd.	found	calcd.	found	
$Co(AcVal)_2 \cdot 2H_2O$	violet	40.85	40.64	6.87	6.61	6.81	6.77	4.62
$Co(AcVal)_2(py)_2 \cdot H_2O$	pink	52.24	52.46	6.59	6.70	10.16	10.13	4.68
$Co(AcVal)_2(3-pic)_2 \cdot 2H_2O$	violet	52.23	52.55	7.09	6.98	9.38	9.29	4.94
$Co(AcVal)_2(4-pic)_2$	pink	55.59	55.38	6.82	6.85	9.98	10.02	4.50
$Co(AcVal)_2(o-phen) \cdot 4H_2O$	pink–violet	49.74	50.13	6.43	5.87	8.93	8.95	5.03
$Ni(AcVal)_2 \cdot 2H_2O$	greenish	40.88	40.52	6.87	6.50	6.82	6.35	3.27
$Ni(AcVal)_2(py)_2 \cdot 2H_2O$	greenish–blue	50.79	51.18	6.40	6.38	9.88	9.71	3.15
$Ni(AcVal)_2(3-pic)_2 \cdot H_2O$	greenish–blue	53.88	53.27	6.96	6.84	9.68	9.61	3.07
$Ni(AcVal)_2(4-pic)_2 \cdot H_2O$	greenish	53.88	52.94	6.96	6.55	9.68	9.72	2.99
$Ni(o-phen)_3(AcVal)_2 \cdot 2H_2O$	pink	63.08	62.40	5.51	5.70	11.78	11.20	3.08
$Zn(AcVal)_2$	white	44.02	43.80	6.34	6.78	7.34	7.28	
$Zn(AcVal)_2(py)_2$	white	53.36	53.28	6.35	6.52	10.38	10.31	
$Zn(AcVal)_2(3-pic)_2 \cdot H_2O$	white	53.27	52.92	6.88	6.97	9.57	9.15	
$Zn(AcVal)_2(4-pic)_2 \cdot H_2O$	white	53.27	52.95	6.88	6.97	9.57	9.56	
$Zn(AcVal)_2(o-phen)$	white	55.55	55.11	5.74	5.99	9.98	10.00	

[a]Abbreviations: AcVal = N-acetyl-DL-valinate ion; py = pyridine; 3- (or 4)pic = 3 (or 4)methylpyridine; o-phen = 1, 10-phenan-throline.

methanolic solution containing metal(II) perchlorate hexahydrate (2 mmol) to a methanolic solution containing N-acetyl-DL-valine (4 mmol), neutralized with a stoichiometric amount of potassium hydroxide in methanol, by filtering the potassium perchlorate precipitated and by adding ethyl ether.

$M(AcVal)_2B_2$ (B = py, 3-pic, 4-pic, o-phen) complexes were separated by adding an excess of base to an ethanolic solution of $M(AcVal)_2 \cdot xH_2O$ complexes and by treating the solution with diethyl ether until complete precipitation of the complexes was obtained.

$Ni(o-phen)_3(AcVal)_2$ complex was obtained by adding to an ethanolic $Ni(AcVal)_2 \cdot 2H_2O$ solution an excess of o-phen until the solution became red. On standing at 3–5 °C for some days the crystalline compound separated.

Physical Measurements

I.r. spectra were recorded with a Perkin-Elmer 180 spectrophotometer in KBr pellets or chloroform (4000–250 cm^{-1}) and in nujol mulls (600–180 cm^{-1}). The room-temperature electronic spectra of the compounds in the solid state or in solution (chloroform or methanol) were recorded with a Shimadzu MPS 50L and with a Perkin-Elmer 551 spectrophotometer. Solid samples were recorded by grinding the complexes using a filter paper as support. The room-temperature magnetic moments were measured with the Gouy method using $Ni(en)_3S_2O_3$ as calibrant and correcting for diamagnetism with the appropriate Pascal constants. ^1H n.m.r. spectra were obtained with a Jeolco model C-60 HL spectrometer for solution in deuterochloroform using $SiMe_4$ as internal standard.

Analyses

Nitrogen, carbon and hydrogen were analysed using a Perkin-Elmer 240 Elemental Analyser by Mr. Giuseppe Pistoni.

Results and Discussion

The analytical results are reported in Table I. The bis(N-acetyl-DL-valinate)metal(II) complexes and the orthophenanthroline adducts are stable in air and soluble in polar organic solvents, while the pyridine adducts, which show a certain degree of hygroscopicity, are soluble in apolar organic solvents.

Solid State Complexes

The room-temperature magnetic moments (Table I) of the complexes are in the range found for high-spin hexacoordinate cobalt(II) and nickel(II) complexes, corresponding to a possible cubic or tetragonal symmetry [7].

TABLE II. Room-temperature Electronic Spectra and Ligand Field Parameters (cm^{-1}) of the Solid Complexes.

	ν_1	ν_3				Dq	B	β^a	ν_2
Co(AcVal)$_2$·2H$_2$O	8000	17300sh	18940	20200sh	21190sh	910	800	0.82	17090
Co(AcVal)$_2$(py)$_2$·H$_2$O	8550	16950sh	19880	21050sh		970	830	0.85	18250
Co(AcVal)$_2$(3-pic)$_2$·2H$_2$O	8130	17300sh	18940	20960sh		920	790	0.81	17360
Co(AcVal)$_2$(4-pic)$_2$	8260		20080	21050sh		940	870	0.90	17670
Co(AcVal)$_2$(o-phen)·4H$_2$O	8420	16950sh	18940	21050sh		950	780	0.80	17340

	ν_1	ν_2		ν_3	Dq	B	β	Dq^b	B^b	$\beta^{a,b}$
Ni(AcVal)$_2$·2H$_2$O	8640	13300sh	14810	25130	865	935	0.89	910	850	0.80
Ni(AcVal)$_2$(py)$_2$·2H$_2$O	9620		15900	26180	960	880	0.83	990	835	0.79
Ni(AcVal)$_2$(3-pic)$_2$·H$_2$O	9520		15820	26180	950	900	0.85	980	840	0.80
Ni(AcVal)$_2$(4-pic)$_2$·H$_2$O	9410		15770	26040	940	910	0.86	980	835	0.79
Ni(o-phen)$_3$(AcVal)$_2$	12580		19230		1260					

[a]The values of the Racah parameter B$_0$ are 971 (Co(II)) and 1056 (Ni(II)) [18].   [b]Calculated from ν_2 and ν_3 bands.

The electronic spectral data and ligand field parameters of the complexes are given in Table II, their room-temperature solid electronic spectra may be assigned in the usual fashion [8], assuming that the stereochemistry "approaches" octahedral. The observed spin-allowed transition in the cobalt(II) and nickel(II) complexes have energies which agree with the secular equation for octahedral metal(II) ions. The energies represent the next electronic transitions from the $^4T_{1g}(F)$ ground state to the next higher excited state, $^4T_{2g}(F)$ (ν_1), $^4A_{2g}(F)$ (ν_2) and $^4T_{1g}(P)$ (ν_3) for the cobalt(II) and from the $^3A_{2g}(F)$ ground state to $^3T_{2g}(F)$ (ν_1), $^3T_{1g}(F)$ (ν_2) and $^3T_{1g}(P)$ (ν_3) higher excited states for the nickel(II).

In the cobalt(II) complexes the ν_1 and ν_3 transitions are assigned with certainty, although the ν_1 is broad and the ν_3 transition shows a multiple structure, whose splitting is probably due to tetragonal distortion or spin—orbit coupling [8]. The ν_2 absorption band, which should appear at approximately twice the energy of the first band and which has been shown to be a two-electron transition and therefore should be weak, is not unambigously assigned as it should appear on the low energy side of the strong intensity ν_3 band. From the ν_1 and ν_3 positions we calculated the Dq and B values together with the ν_2 band, which is found in the 17090–18250 cm^{-1} range.

The low energy band, of the nickel complexes is broad, indicating tetragonal distortion. The Dq and B values calculated using only the sharp ν_2 and ν_3 bands are different from those calculated by using ν_1, ν_2 and ν_3. In particular the B values, calculated with ν_1 (= 10Dq), ν_2 and ν_3 are greater than those calculated with only the sharp ν_2 and ν_3 transitions, confirming that some distortion of the O$_h$ symmetry is present [9]. The Dq and B values of the hydrate

bis(N-acetyl-DL-valinate)cobalt(II) and nickel(II) closely resemble those found for MO$_6$ chromophore [10, 11] indicating further a ligand field strength of the N-acetyl-DL-valine similar to that of the water.

The Dq values of the adducts are intermediate between the values found for MO$_6$ and MN$_6$ chromophores [10, 11]. This indicates the presence of oxygen and nitrogen in the coordination sphere of the metal(II) ion, with the probable presence of MO$_4$-N$_2$ chromophore, the amines being coordinated. In particular the ligand field strength order py > 4-pic or 3-pic reverses the basicity order of the amine [12] and may be attributed to steric intereference, which modifies the inductive effect of the 3- (or 4-) methyl group.

The presence of NiN$_6$ chromophore is, instead, suggested by the electronic spectrum of the tris(o-phenanthroline nickel(II))bis(N-acetyl-DL-valine) complex, which is the typical spectrum of the tris(o-phenanthroline)nickel(II) cation [13], suggesting that the amino acid is in the ionic form.

By comparing the Dq values of the present hydrate bis(N-acetyl-DL-valinate)metal(II) complexes and those reported for similar hydrate bis(N-substituted aminoacid)metal(II) complexes, we obtain for both cobalt(II) and nickel(II) a ligand field strength order of this type: N-benzoyl-glycine (984^a, 890^b) > N-acetyl-glycine (945^a, 880^b) > benzoyl-β-alanine (933^a, 880^b) > α, N-benzoyl-DL-alanine (922^a, 870^b) > N-acetyl-L-alanine (918^a) > N-acetyl-DL-valine (910^a, 865^b), [a (= Dq for the Co(II)) and b (= Dq calculated from ν_1 for the Ni(II)) are in cm^{-1}].

As a general consideration we may observe that the β-amino acids and the benzoyl derivatives have a greater ligand field strength than the α-amino acids and the acetyl derivatives, respectively. The inductive effect of the R group on the nitrogen atom clearly

TABLE III. More Relevant Infrared Bands (cm^{-1}) of the Solid Complexes.

	$\nu(NH)$	$\nu(\overset{+}{N}H_2)$	$\nu(CO)_{ket}$	$\nu(COO)_{asym}$	$\nu(COO)_{sym}$	ν	$\delta(NH)$
AcValH[a]	3364s	2400–2800sb	1592vs	1710vs	1212vs	498	1540vs
AcValNa	3298s		1655vs	1588vs	1407vs	181	1545vs
AcValK	3280msb		1640s	1587vs	1394vs	193	1540sh
$Co(AcVal)_2 \cdot 2H_2O$	3300sb		1650sh	1595vs	1418vs	177	1540sh
$Co(AcVal)_2(py)_2 \cdot H_2O$	3300s			1620vs	1400s	220	1530s
$Co(AcVal)_2(3\text{-pic})_2 \cdot 2H_2O$	3300s		1650sh	1620vs	1402vs	218	1530sb
$Co(AcVal)_2(4\text{-pic})_2$	3338m 3284s		1640sh	1580vs	1408vs	172	1540s
$Co(AcVal)_2(o\text{-phen}) \cdot 4H_2O$	3300mb		1650sh	1630vs	1420vs	210	1540sh
$Ni(AcVal)_2 \cdot 2H_2O$	3335sb		1655sh	1595vsb	1415vs	180	1540sh
$Ni(AcVal)_2(py)_2 \cdot 2H_2O$	3370, 3308ms		1650sh	1630vs	1403s	227	1530s
$Ni(AcVal)_2(3\text{-pic})_2 \cdot H_2O$	3310, 3295s		1645sh	1618vs	1400vs	218	1525sh
$Ni(AcVal)_2(4\text{-pic})_2 \cdot H_2O$	3380ms 3300sh		1650sh	1612vs	1400s	212	1530s
$Ni(o\text{-phen})_3(AcVal)_2$	3400ms 3300sh		1645s	1592vs	1421vs	171	1515s
$Zn(AcVal)_2$	3300s		1650sh	1610vs	1415s	195	1540sh
$Zn(AcVal)_2(py)_2$	3310, 3270s		1655sh	1645vs	1421vs	224	1550sh
$Zn(AcVal)_2(3\text{-pic})_2 \cdot H_2O$	3288s		1650sh	1600vs	1382vs	218	1530s
$Zn(AcVal)_2(4\text{-pic})_2 \cdot H_2O$	3272s		1658s	1598vs	1400vs	198	1535s
$Zn(AcVal)_2(o\text{-phen})$	3295ms		1650vs	1620vs	1420vs	200	1515vs

[a]The amino acid shows broad bands at 2400–2800 cm^{-1}, which disappear in the salts, indicating that the amino acid is partially present in the zwitterionic form.

affects the coordination properties of the carboxylate group, the ligand strength of which appears more weakened if R = acetyl than if R = benzoyl group.

The assignments of the more relevant infrared bands (Table III) for emphasizing the amino acid coordination are made by comparing the amino acid, its sodium and potassium salts and their deuterated analogues. In all the solid complexes we may exclude the coordination of the peptide group to the metal as the NH and CO (ketonic) stretching frequencies shift to higher energies and the NH bending vibration to lower energies with respect to the free ligand. This confirms the spectroscopic results which indicated a coordination of the amino acid toward the carboxylate group.

The carboxylate group shows two bands, an intense antisymmetric carboxylate stretching and a symmetric stretching. Trends in the positions of and separation between these bands are the most useful tools in assigning structures from infrared spectra, although some difficulty in assignment may occur as their position and separation depend upon the electronic nature of the group R, the properties of the central metal ion and possibly the identity of the trans-ligands present, and as the band at about 1400 cm^{-1}, which is usually designated as the symmetric carboxylate stretch, is due to mixing of the C–O with C–C symmetric stretching [14]. It is known that the

free carboxylate group has C_{2v} symmetry, which is retained when it acts as a bidentate chelate (or as bridging group) [15, 16], for which the CO_2 stretching frequencies are not expected to be greatly different from those of the free carboxylate spectrum. When it acts as a monodentate ligand the carboxylate assumes a C_s symmetry and, as the C–O bonds become inequivalent, the antisymmetric stretching is expected to increase with respect to the free ion, as the vibration takes on more ketonic character, whereas the symmetric stretching decreases. Hence a large splitting of the OCO-stretching frequencies is often an indication of monodentate coordination. Our assignment of mono- or bi-dentate carboxylate group is based on these criteria. We exclude the presence of bridging carboxylate group of the type found in copper acetate monohydrate, whose i.r. bands are expected in the same position, as the presence of this type of coordination produces metal–metal interactions which generate "anomalous" magnetic moments. The reported values of $\Delta\nu(\nu(OCO)_{asym} - \nu(OCO)_{sym})$ for the sodium and potassium salts and for the $Ni(o\text{-phen})_3(AcVal)_2$ complexes give a range of 171–193 cm^{-1} which typify ionic N-acetyl-DL-valinate spectra. By comparing these values with those found for all the complexes, we may suggest that the carboxylate group acts as a bidentate ligand in all cases. In the bis-

TABLE IV. Electronic Spectra and Ligand Field Parameters (cm^{-1}) of the Complexes Solution.[a]

	Solvent	ν_1	ν_3	D_q	B	β	ν_2
Co(AcVal)$_2$·2H$_2$O	Methanol	8000(3)	19230(13) 20580sh(~10) 21280sh(~8)	910	820	0.84	17100
Co(AcVal)$_2$(o-phen)·4H$_2$O	Methanol	8850(5)	19230sh(~28) 21730sh(~38)	1000	770	0.80	18830
Co(AcVal)$_2$(py)$_2$·H$_2$O	Chloroform	8420(5)	19530(42) 20280sh(~40) 21050sh(~38)	955	815	0.84	17970
Co(AcVal)$_2$(3-pic)$_2$·2H$_2$O	Chloroform	8330(7)	19230(45) 20160sh(~39) 21050sh(~30)	945	800	0.80	17780
Co(AcVal)$_2$(4-pic)$_2$	Chloroform	7270sh(~7) 8510(8)	17940sh(41) 18980(61) 21050sh(~35)	962	770	0.80	18130

	Solvent	ν_1	ν_2	ν_3	D_q	B	β	$D_q{}^{b}$	B^{b}	β^{b}
Ni(AcVal)$_2$·2H$_2$O	Methanol	8660(6)	13510sh(~4) 14930(5)	25000(13)	865	930	0.88	920	830	0.79
Ni(o-phen)$_3$(AcVal)$_2$	Methanol	11430sh(~5) 12500(6)	19230(12)		1250					
Ni(AcVal)$_2$(py)$_2$·2H$_2$O	Chloroform	9280(6)	13330sh(~3) 15670(8)	25970(18)	930	920	0.87	970	840	0.80
Ni(AcVal)$_2$(3-pic)$_2$·H$_2$O	Chloroform	9090(5)	13330sh(~4) 15580(9)	25970(18)	910	950	0.90	960	850	0.80
Ni(AcVal)$_2$(4-pic)$_2$·H$_2$O	Chloroform	9220(6)	15690(10)	25970(18)	920	930	0.88	970	840	0.80

[a]The concentrations of the solutions are in the 4–7 × 10^{-2} M range. In parenthesis are reported ϵ (1 mol^{-1} cm^{-1}). [b]Calculated from ν_2 and ν_3 bands.

TABLE V. Infrared Spectra (cm^{-1}) of the Amine Adducts in Chloroform (4–7 × 10^{-2} M).

	ν(NH)	ν(CO)$_{ket}$	ν(COO)$_{asym}$	ν(COO)$_{sym}$	$\Delta\nu$	δ(NH)
Co(AcVal)$_2$(py)$_2$·H$_2$O	3418m	1655sh	1635vs	1408vs	227	1500s
Co(AcVal)$_2$(3-pic)$_2$·2H$_2$O	3420m	1655sh	1633vs	1410vs	223	1502s
Co(AcVal)$_2$(4-pic)$_2$	3420m	1652sh	1615vs	1410vs	205	1498s
Ni(AcVal)$_2$(py)$_2$·2H$_2$O	3415m	1650sh	1638vs	1408s	220	1500s
Ni(AcVal)$_2$(3-pic)$_2$·H$_2$O	3410m		1638vs	1410vs	218	1505s
Ni(AcVal)$_2$(4-pic)$_2$·H$_2$O	3410m	1645sh	1605vs	1412s	183	1510s
Zn(AcVal)$_2$(py)$_2$	3422m	1650sh	1620vs	1390s	230	1502s
Zn(AcVal)$_2$(3-pic)·H$_2$O	3420m	1655sh	1622vs	1390s	232	1502s
Zn(AcVal)$_2$(4-pic)·H$_2$O	3420m	1650sh	1617vs	1390s	227	1500s

TABLE VI ^{1}H n m r Results for the Ligands and Some Zinc(II) Adducts

	Solvent	δ/p p m						cps	
		CH$_3$\C/CH$_3$	CH$_3$CO	C\CH/C	CH$_3$-py	CHCOO	NH	J$^{HH}_{CHCH}$	J$^{HH}_{HNH}$
AcValH	D$_4$-methanol	1 00	2 05	2 16		4 31		5 25	
AcValK	D$_4$-methanol	0 94	2 00	2 10		4 11		5 25	
Zn(AcVal)$_2$(py)$_2$	D-chloroform	0 90	2 00	a		4 53	6 59	4 53	8 25
Zn(AcVal)$_2$(3-pic)$_2$·H$_2$O	D-chloroform	0 91	2 01	a	2 40	4 44	6 68	4 53	9 00
Zn(AcVal)$_2$(4-pic)$_2$·H$_2$O	D-chloroform	0 83	2 00	a	2 43	4 51	6 46	4 50	8 25

^{a}Obscured by the CH$_3$CO

(N-acetyl-DL-valinate) complexes of the divalent cobalt, nickel and zinc, as the Δν values are in the range reported for the free ligand ion, we may suppose that the carboxylate group acts as "symmetrical" chelating ligand

The Δν values of the amines are greater than those reported for the aquo complexes The transfer of electron density, due to additional ligands in axial position, lowers the metal–N-acetyl-DL-valinate coordination strength This effect decreases in the order py > 4-pic > 3-pic, which is the same sequence found for the Dq values, confirming that steric effects prevail on inductive effects The coordination of the amines is evidentiated by the shift of the bands in the 800–500 cm^{-1} region in the aromatic heterocyclic amine adducts with respect to free ammines [17]

Solution Complexes

The electronic spectra of all the complexes (Table IV) in solution also suggest the presence of hexacoordinated metal(II) As the electronic and infrared spectra (Table IV and V) of the solution complexes are very similar to those of the solid complexes, similar conclusions may be suggested

The only relevant difference between the solid and solution complexes may be observed in the infrared spectra in the ν(NH) and δ(NH) positions which in the solution complexes are shifted to higher and lower energies, respectively, with respect to the solid complexes, indicating that in the packing within the crystal the NH group of the amino acid is involved in some hydrogen bonds which are removed in chloroform solution

The ^{1}H n m r spectra (Table VI) of the zinc(II) compounds agree very well with a symmetrical structure also in the case of substituted pyridine ligands, their spectra being simple and similar to those of the N-acetyl-DL-valine and its potassium salt The ^{1}H n m r spectra also confirm the coordination of the N-acetyl-DL-valine ion toward the carboxyl

group, as the αCH group is greatly affected by coordination.

Furthermore, the ^{1}H n m r spectra of the pyridine and methyl-pyridine adducts in D-chloroform show a splitting of the NH resonance in two bands and of the two CHCOO resonances in four bands The splitting disappears on adding D$_4$-methanol, indicating a coupling of the CHNH group, which confirms that the NH group is not involved in hydrogen bonding in chloroform solution

Acknowledgments

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