Infrared Band Assignments for L-Alanine and the Nickel(II) and Copper(II) Complexes of L- and β-Alanine

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The i.r. spectra of L-alanine, its ^{18}O- and ^{15}N-labelled analogues, hydrated and anhydrous $[Ni(L\text{-}AlaO)_2]$, anhydrous *trans*-$[Cu(L\text{-}AlaO)_2]$ (L-AlaO = L-alaninate anion), their ^{18}O- and ^{15}N-labelled analogues, *trans*-$[Ni(\beta\text{-}AlaO)_2(OH_2)_2]$, and $[Cu(\beta\text{-}AlaO)_2]$ (β-AlaO = β-alaninate anion) have been recorded in the 150—4 000 cm^{-1} region. The effects of the isotopic substitutions indicate the need for revision of certain band assignments in the spectra of L-Ala and its complexes. Band assignments in the spectra of the β-AlaO complexes have been accomplished by comparison with the spectrum of *trans*-$[Ni(GlyO)_2(OH_2)]$ (GlyO = glycinate anion).

THE majority of bands in the i.r. spectrum of DL-alanine (DL-Ala) have been assigned on the basis of a normal-co-ordinate treatment and C- and N-deuteriation studies.[1] These results were substantiated by a subsequent ^{15}N study [2] (500—1 700 cm^{-1}) except that the absorption at 540 cm^{-1}, previously assigned [1] as a CO_2^- bending mode, was reassigned [2] as a CCN bending vibration. C- and N-Deuteriation studies [3] (700—1 700 cm^{-1}) of L-alanine (L-Ala) supported these assignments. We have determined the spectra of ^{15}N- and ^{18}O-labelled L-Ala in the 150—1 700 cm^{-1} region. The results, which provide evidence for vibrational coupling, suggest that some modification of the previous assignments is necessary.

Although a normal-co-ordinate analysis has been performed on metal(II) complexes of DL-Ala and assignments

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[1] S. Suzuki, T. Oshima, N. Tamiya, K. Fukushima, T. Shimanouchi, and S. Mizushima, *Spectrochim. Acta*, 1959, **15**, 969.

[2] M. Tsuboi, T. Takenishi, and A. Nakamura, *Spectrochim. Acta*, 1961, **17**, 634.

[3] T. Oshima and N. Tamiya, *Spectrochim. Acta*, 1961, **17**, 384.

proposed for most of the observed bands,[4] some workers [5,6] have preferred to base their assignments of the i.r. spectra of the complexes of amino-acids on the results of a more sophisticated normal-co-ordinate treatment of glycine (Gly) complexes.[7] We have recently shown,[8,9] by means of isotopic labelling of the chelate ring, that many of the assignments which resulted from normal-co-ordinate analyses [7,10] of metal(II) glycinates required substantial revision. Since the normal-co-ordinate treatment of complexes of DL-Ala was essentially based [4] on the incorrect results [10] obtained for complexes of Gly (see ref. 8), it seemed appropriate to extend our study of the i.r. spectra of complexes of amino-acids to include complexes of ^{15}N- and ^{18}O-labelled L-Ala in order to make more reliable assignments of some of the internal ligand and metal–ligand vibrations that involved movement of the labelled atoms. In addition, the i.r. spectra of the hydrated nickel(II) and anhydrous copper(II) complexes of β-Ala have been assigned by comparison with those proposed [8] for *trans*-[Ni(GlyO)$_2$(OH$_2$)$_2$] (glyO = glycinate).

EXPERIMENTAL

The complexes were prepared by published methods.[4-6,11] The isotopically substituted complexes were prepared from ^{15}N-L-alanine of 96 atom-% purity supplied by Merck, Sharpe, and Dohme Ltd. and ^{18}O-L-alanine of 77 atom-% purity supplied by Prochem Ltd. Purity was established by microanalysis. Infrared spectra were recorded for Nujol or hexachlorobutadiene mulls between CsI plates (or, below 250 cm^{-1}, between polyethylene plates) on a Perkin-Elmer 180 spectrophotometer.

RESULTS AND DISCUSSION

I.r. Spectrum of L-*Alanine*.—The ^{15}N and ^{18}O isotopic shifts (Δν) are recorded in Table 1. Our data on ^{15}N-L-Ala are in good agreement with those reported [2] for ^{15}N-DL-Ala. The assignments in Table 1 essentially follow previous reports.[1-3] Only bands for which different or modified assignments are suggested, as a result of the ^{18}O data, will be discussed.

The ^{18}O shift of the NH$_3^+$ degenerate deformation at 1 621 cm^{-1} suggests considerable coupling of this vibration to the CO$_2^-$ asymmetric stretch. Of the three ^{18}O-sensitive bands at 1 412, 1 362, and 1 307 cm^{-1}, only that at 1 412 cm^{-1} has previously been assigned [1-3] to the CO$_2^-$ symmetric stretch. Our results indicate that this vibration is possibly distributed over all three of these bands. Since the band at 1 412 cm^{-1} is also shifted [3] by deuteriation of the α-C atom, it is assigned to the CO$_2^-$ symmetric stretch + C–H bend or C–CO$_2^-$ stretch. The band at 1 362 cm^{-1} which is sensitive to deuteriation of the methyl group [3] is assigned as the CH$_3$ symmetric deformation + CO$_2^-$ symmetric stretch. Deuteriation of the α-C atom has led to the assignment [3] of the band at 1 307 cm^{-1} as the C–H bend. We have reassigned this band to the C–H bend + CO$_2^-$ symmetric stretch. It is possible that the C–H deformation vibrations at 1 362 and 1 307 cm^{-1} are coupled to the C–CO$_2^-$ stretch. A similar assignment has been proposed for a band in this region of the i.r. spectrum of Gly.[12] Carbon-13 labelling would further clarify these assignments.

TABLE 1

Wavenumbers (cm^{-1}), ^{15}N-induced shifts (Δν^{15}N),[a] ^{18}O-induced shifts (Δν^{18}O),[a] and assignments in the i.r. spectrum of L-alanine (all the other shifts above 600 cm^{-1} were < 1.5 cm^{-1} and below 600 cm^{-1} were < 1 cm^{-1})

ν	Δν^{15}N	Δν^{18}O	Assignments
1 621	1.5	9.5	NH$_3^+$ degenerate deformation + CO$_2^-$ asym. stretch
1 590		13	CO$_2^-$ asym. stretch
1 519			
1 505	3		NH$_3^+$ sym. deformation
1 455			CH$_3$ degenerate deformation
1 412		9.5	CO$_2^-$ sym. stretch + C–H bend or C–CO$_2$ stretch
1 362		8	CH$_3$ sym. deformation + CO$_2^-$ sym stretch
1 307		11	CH bend + CO$_2^-$ sym. stretch
1 237	3		NH$_3^+$ rock + CH$_3$–C–N asym. stretch
1 152	4	1.5	NH$_3^+$ rock + CH$_3$ rock + CH$_3$–C–N asym. stretch + CO$_2^-$ sym. stretch
1 114	2	3	
1 014	2.5		CH$_3$ rock + CH$_3$–C–N sym. stretch
919	3	7.5	CH$_3$–C–N sym. stretch + CO$_2^-$ scissor
850	2.5	15.5 [b]	CO$_2^-$ scissor + CH$_3$–C–N sym. stretch
772		5.5	CO$_2^-$ scissor + C–C stretch
649		15	CO$_2^-$ rock
539	2	14	CO$_2^-$ wag + CCN bend
486	1		NH$_3^+$ torsion
410	2.5	3.5	NCCO deformation
323	3	3	
293		6	CCO deformation
258		3	
210			skeletal torsion
169			CH$_3$ torsion

[a] All the shifts are to lower wavenumber. [b] Average shift to doublet at 838 and 831 cm^{-1}.

The mixed vibrations [3] at 1 152 and 1 114 cm^{-1} appear to have CO$_2^-$ or C–CO$_2^-$ stretching character. Both the bands at 919 and 850 cm^{-1} were assigned [3] as CH$_3$–C–N stretches coupled to C–C stretching. We suggest that, because of its large ^{18}O shift, the band at 850 cm^{-1} is more reasonably assigned as the CO$_2^-$ scissoring mode and that the ^{15}N sensitivity is the result of coupling to the CH$_3$–C–N symmetric stretch. In the spectrum of Gly [12] the CO$_2^-$ scissoring vibration occurs at 894 cm^{-1}. The smaller ^{18}O shift of the band at 919 cm^{-1} indicates it is a purer CH$_3$–C–N stretching mode coupled to the CO$_2^-$ scissoring vibration. In view of our reassignment of the band at 850 cm^{-1}, the band at 772 cm^{-1} is reassigned as CO$_2^-$ scissoring + C–C stretching. The magnitude of its

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^{18}O shift shows that this band is not a pure CO_2^- bend as previously suggested.[3]

The absorption at 539 cm^{-1} was assigned on the basis of a normal-co-ordinate treatment to a CO_2^- bending vibration [1] but subsequently reassigned, as a result of its ^{15}N sensitivity, to a CCN bend.[2] The ^{18}O shift confirms that this band does have CO_2^- bending character. This band is therefore assigned as predominantly a CO_2^- wag coupled to a CCN bend. It is generally agreed [1,4] that the bands below 450 cm^{-1} are torsional and deformational modes; however, previous assignments [1,4] of the absorptions at 410, 323, and 293 cm^{-1} as CCCN deformations do not agree with the observed ^{18}O- and ^{15}N-isotopic shifts. These bands are reassigned as NCCO and CCO deformations.

TABLE 2

Wavenumbers (cm^{-1}), ^{15}N-induced shifts ($\Delta\nu^{15}N$),[a] ^{18}O-induced shifts ($\Delta\nu^{18}O$),[a] and assignments in the i.r. spectra of the anhydrous nickel(II) and copper(II) and the hydrated nickel(II) complexes of L-alanine (all the other shifts above 600 cm^{-1} were <1.5 cm^{-1} and below 600 cm^{-1} were <1 cm^{-1})

[Ni(L-AlaO)$_2$]			[Cu(L-AlaO)$_2$]			[Ni(L-AlaO)$_2$(OH$_2$)$_2$]·H$_2$O			
ν	$\Delta\nu^{15}N$	$\Delta\nu^{18}O$	ν	$\Delta\nu^{15}N$	$\Delta\nu^{18}O$	ν	$\Delta\nu^{15}N$	$\Delta\nu^{18}O$	Assignments[b]
1 588	4	11	1 619	2	21	1 580		15	C=O stretch
1 570 (sh)	4[c]		1 573	3		1 606 (sh)	d	d	NH_2 scissor
1 477	2	2	1 468	e	f				CH_3 deg. def. + C=O stretch + NH_2 scissor
1 462			1 463						
1 409			1 453			1 461			CH_3 deg. def.
1 402		12	1 400		g	1 417		15.5	C–O stretch
			1 390	h		1 379			
			1 382						
1 368		i				1 372		2.5	CH_3 sym. def. + C–O stretch[j]
1 365			1 361	1.5	10	1 361	2	5	
1 341		3	1 351						CH bend
1 327	2		1 339	2		1 349	1.5		NH_2 twist
1 308		6	1 306		9	1 308		5	CH bend + C–O stretch
1 295		4.5	1 296	1.5	13	1 298	1.5	4	
1 232			1 247						CH_3 rock
1 206	2	3.5	1 220		2	1 224	2	2	CH_3 rock + C–O stretch[j]
1 134		2.5							
			1 116	6	4.5	1 171	2.5	2	NH_2 wag + C–O stretch
			1 147	5	4.5	1 151	2.5	2.5	
1 113	3					1 122	2.5		NH_2 wag
1 089	7	2	1 121	6.5	1.5	1 085	7.5	1.5	C–N stretch
1 036	4.5		1 078	3	2.5	1 046	2	2	C–N stretch + C–O stretch
1 008	3	3.5	1 027	2	2.5	1 021	1.5		
925	5	6.5	926	4.5	5.5	931	4	8.5	C–N stretch + CO_2 scissor
859	2.5	20	858	3.5	k	859	3	16	CO_2 scissor + C–N stretch
			851	2.5					
777		6.5	786		8	785		11	CO_2 scissor + C–C stretch
767		5.5	768		5				
712	1.5	14	708	1.5	11	656	2	10	CO_2 rock
						614		2	OH_2 rock
632	5.5		673	5	2	579	5		NH_2 rock
603	3.5	7	605	2.5	12				CO_2 wag + ring def.
569	5.5	12.5	574	7.5	7	552	3	8	CO_2 wag + M–N stretch
462	4.5	5	489	6.5	6.5	466	6		M–N stretch + (M–O stretch)[l]
402	2.5	5.5	398	2	4				ring def.
376	1.5	4.5	385 (sh)	c	c	378		3	M–O stretch + ring def.
344		7	362		4.5	316	d	5	M–O stretch
326		1	335	2	2.5	304	d	4	M-ligand bend
285		2	322	1	1				
236		7	302		7				M · · · O stretch
			279	2	5				
211		5	207	1.5	9				
			175		5				
191						226			
						180			

[a] All the shifts are to lower wavenumber. [b] Predominant mode. [c] Best estimate of shoulder. [d] Shifts cannot be determined. [e] Singlet at 1463 cm^{-1}. [f] Singlet at 1 461 cm^{-1}. [g] Singlet at 1 390 cm^{-1}. [h] Singlet at 1 386 cm^{-1}. [i] Singlet at 1 363 cm^{-1}. [j] See text. [k] Singlet at 837 cm^{-1}. [l] Plus M–O stretch for anhydrous complexes.

I.r. Spectra of Nickel(II) *and Copper*(II) *Complexes of* L-*Alanine*.—The isotopic shifts ($\Delta\nu$) recorded in Table 2 reveal the extent to which vibrational mixing is present in the i.r. spectra of complexes of L-Ala; several bands are sensitive to both forms of labelling. Assignments proposed in Table 2 are based on the effects of the isotopic substitutions and by comparison with assignments proposed for L-Ala and for complexes of Gly.[8] In listing the assignments we infer that the band originates predominantly from that mode, although other vibrations appear to contribute to the vibrational energy.

The assignments [4] of the C=O and C–O stretching and the NH_2 scissoring modes are substantiated by the observed isotopic shifts. Absorptions between 1 480 and 1 200 cm^{-1} ascribed [4] to the CH_3 rocking and deformation modes and the CH bending mode are in many cases coupled to vibrations involving the carbonyl groups.

As in the case of the free ligand these vibrations may involve the C=O, C–O, or C–CO_2 stretches. In the spectrum of *trans*-[$Ni(GlyO)_2(OH_2)_2$], coupling of the CH_2 deformations to the C–O stretch rather than the C–CO_2 stretch was inferred by the magnitudes of the observed ^{13}C shifts.[8] The band which is the most ^{15}N sensitive occurs near 1 100 cm^{-1} and is assigned to the C–N stretch.

The normal-co-ordinate analysis of these complexes led to the assignment of all the CO_2 bending vibrations in the region below 790 cm^{-1}.[4] Our results establish that the purest CO_2 scissoring vibration occurs near 850 cm^{-1}, in the same region as it is observed in the spectrum of the ligand. The higher frequency band near 925 cm^{-1} shows sufficient ^{15}N sensitivity to suggest coupling of the CO_2 scissoring and C–N stretching vibrations. Three bands between 790 and 700 cm^{-1} are ^{18}O sensitive. The most sensitive absorption near 700 cm^{-1} is assigned as the CO_2 rock, while the two at higher frequency which show much smaller ^{18}O shifts are assigned as the CO_2 rock + C–C stretch.

The CO_2 wagging modes appear between 600 and 550 cm^{-1}. That at 600 cm^{-1} is assigned to CO_2 wagging + ring deformation. Support for this band being coupled to a ring-deformation vibration is provided by the fact that a band in this region in the spectrum of *trans*-[$Ni(GlyO)_2(OH_2)_2$] is sensitive to isotopic labelling of every atom of the chelate ring.[8] The relatively large ^{15}N shifts of the band near 560 cm^{-1} strongly support its assignment to the CO_2 wag + M–N stretch.

In the anhydrous complexes the weak absorption near 470 cm^{-1} is sensitive to ^{15}N and ^{18}O substitution and is therefore assigned as M–N + M–O stretching. The corresponding band in the hydrated complex shifts only on ^{15}N substitution and is assigned to M–N stretching. This band was not reported in the normal-co-ordinate treatment of these complexes.[4] It is interesting to note that the Cu–N stretch of *trans*-[$Cu(L\text{-}AlaO)_2$] has been empirically assigned to the 489 cm^{-1} absorption.[5] The assignment of the M–O stretches near 350 cm^{-1} is based on ^{18}O and metal sensitivity, that near 380 cm^{-1} being assigned as M–O stretch + ring deformation while the one at lower frequency, which shows the largest ^{18}O and metal sensitivity, is assigned as the 'purest' M–O stretch. The band at 400 cm^{-1} which shows no metal sensitivity is assigned as a ring deformation. The metal sensitivity in the order Cu > Ni is associated with the higher crystal-field stabilisation energy of Cu^{II} relative to that of Ni^{II} and has been found to pertain to the metal–ligand bands of numerous complexes.[13] The metal–ligand bends occur near 300 cm^{-1}. The above assignments of the metal–ligand stretches and bends are entirely consistent with those proposed[8] for *trans*-[$Ni(GlyO)_2(OH_2)_2$].

The spectrum of the anhydrous nickel(II) complex shows two further ^{18}O-sensitive bands at 236 and 211 cm^{-1} while that of the copper(II) complex shows additional ^{18}O-sensitive bands at 302, 279, 207, and 175 cm^{-1}. Since it has been shown crystallographically[14] that the carbonyl group enters into Cu ··· O bridging in tetragonally distorted, six-co-ordinate, [$Cu(L\text{-}AlaO)_2$], we propose that these bands be assigned as M ··· O stretching. Support for this assignment is provided by the absence of these bands in the hydrated nickel complex where the fifth and sixth co-ordination sites are occupied by water molecules. The apparent splitting of the two bands observed for the anhydrous nickel(II) complex into four bands for the copper(II) complex could well be a consequence of the tetragonal distortion. Splitting of this nature of the metal–ligand bands, as a result of tetragonal distortion, has been well substantiated for many copper complexes.[13] In view of the fact that the C=O stretch occurs at a much lower frequency in the spectrum of the anhydrous nickel(II) complex we suggest that there is a much closer M ··· O interaction and hence a more regular octahedral structure for this complex than in the copper(II) case.

TABLE 3

Wavenumbers (cm^{-1}) and assignments in the i.r. spectra of [$Ni(\beta\text{-}AlaO)_2(OH_2)_2$] and [$Cu(\beta\text{-}AlaO)_2$]

[$Ni(\beta\text{-}AlaO)_2(OH_2)_2$]	[$Cu(\beta\text{-}AlaO)_2$]	Assignments
3 316	3 260	N–H asym. stretch
3 266	3 170	N–H sym. stretch
1 615	1 617	NH_2 scissor
1 600	1 575	C=O stretch
1 460	1 477	CH_2 scissor + C–O stretch
1 415	1 410	C–O stretch + C–C stretch
1 384	1 380	
1 322	1 322	CH_2 wag + C–O stretch
1 264	1 279	CH_2 wag + NH_2 twist
1 168	1 180	CH_2 twist + C–C stretch
1 127	1 146	NH_2 wag
1 080	1 089	C–N stretch
1 008	1 036	CO_2 scissor + C–C stretch
977	974	
896	888	CO_2 scissor + CH_2 rock
875	867	
838		OH_2 rock
722	721	CO_2 rock + CH_2 rock + NH_2 rock
652	701	NH_2 rock
617	625	CO_2 wag + ring deformation
	600	
509	517	CO_2 wag + M–N stretch
434	488	M–N stretch + M–O stretch
367	404	M–O stretch
334		Ni–OH_2 stretch
305	324	O–M–O bend
283	281	ring deformation
243		OH_2 libration or hydrogen-bond stretch
207	259	N–M–O bend
171	180	OH_2 libration or hydrogen-bond stretch
164		

The assignments proposed in this work are considerably different from those obtained for the normal-co-ordinate treatment (based on a four-co-ordinate model) of the complexes of DL-Ala in which the M–N stretch and M–O stretch were assigned near 330 cm^{-1} and below 200 cm^{-1}, respectively.[4] In addition, other bands below 700 cm^{-1} were incorrectly assigned as a result of incorrect assignments obtained for the ligand.[4,5]

I.r. Spectra of Nickel(II) *and Copper*(II) *Complexes of β-Alanine*.—Table 3 lists the i.r. bands and assignments for *trans*-[$Ni(\beta\text{-}AlaO)_2(OH_2)_2$] and [$Cu(\beta\text{-}AlaO)_2$]. The

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assignments are based on those obtained for isotopically labelled *trans*-[Ni(GlyO)$_2$(OH$_2$)$_2$]. This procedure is entirely reasonable because of the striking resemblance between the spectra of the complexes of β-Ala and Gly because of their structural similarities.[15,16] From the spectral similarities, we suggest that [Cu(β-AlaO)$_2$] also has a *trans* configuration.

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