Infrared Band Assignments of the Nickel(II) Complex of Glycine

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The i.r. spectra of *trans*-[Ni(gly)$_2$(H$_2$O)$_2$] (gly = glycinate anion) and its ^{18}O-, ^{15}N-, 1-^{13}C-, and 2-^{13}C-labelled analogues were measured in the 150—4 000 cm^{-1} region. The effects of isotopic substitutions indicate the need for revision of certain assignments of internal ligand vibrations and allow the assignment of the nickel–ligand vibrations.

THERE is general agreement on the frequency ranges in which the internal ligand vibrations in the i.r. spectra of amino-acid complexes occur.[1-3] Two different opinions,[4,5] which have originated from independent normal co-ordinate treatments performed on complexes of glycine, exist on the assignment of the metal–ligand stretching vibrations of *trans*-[Ni(gly)$_2$(H$_2$O)$_2$]. The first normal co-ordinate analysis [4] of the region 670—270 cm^{-1}, based on the view [6] that the M–O bonds were essentially ionic, assigned the Ni–N stretching vibration at 283 cm^{-1}. An extension [7] of this analysis resulted in the assignment of a band near 150 cm^{-1} as the M–O stretching vibration of the corresponding Pt$^{\mathrm{II}}$, Pd$^{\mathrm{II}}$, and Cu$^{\mathrm{II}}$ complexes. A more sophisticated normal co-ordinate treatment [5] of the range 4 000—250 cm^{-1} led to the assignment of the Ni–N stretching vibration to the weak 437 cm^{-1} absorption, which had not been observed in the former analyses,[4] and to the assignment of the Ni–O(gly) stretching vibration, mixed with Ni–N stretching character, at 290 cm^{-1}. There has been general acceptance of these latter assignments which have been used [2,3] as a guide to the assignment of metal–ligand vibrations in other metal complexes of amino-acids.

Since isotopic substitution of the ligand atoms has been shown [8,9] to yield reliable assignments it seemed appropriate to study the effects of ^{15}N- and ^{18}O-labelling in order to clarify the assignments of the metal–ligand vibrations in *trans*-[Ni(gly)$_2$(H$_2$O)$_2$]. In addition, the carbon atoms of the chelate ring were isotopically labelled to verify assignments [5] of the internal ligand vibrations.

EXPERIMENTAL

The complexes were prepared according to the method used by Stosick.[10] The isotopically substituted complexes were prepared from ^{15}N-, ^{18}O-, 1-^{13}C-, and 2-^{13}C-glycine of 95, 78, 92, and 93 atom-% purity, respectively, supplied by Prochem Ltd. Purity was established by microanalysis. I.r. spectra were determined in Nujol or hexachlorobutadiene mulls between CsI plates (or below 250 cm^{-1}, between polyethylene plates) on a Perkin-Elmer 180 spectrophotometer.

RESULTS AND DISCUSSION

The isotopic shifts ($\Delta\nu$) recorded in the Table reveal the extent to which vibrational mixing is present in the i.r. spectrum of *trans*-[Ni(gly)$_2$(H$_2$O)$_2$]; several bands are sensitive to all forms of labelling. As a result of hydrogen bonding,[8,11] the N–H stretching vibrations near 3 300 cm^{-1} are shifted by *ca.* 1/2 the calculated [8] value. The C–H stretches do, however, exhibit the expected [8] shifts on 2-^{13}C-substitution. The strong, broad absorption at 1 590 cm^{-1} is assigned, on the basis of the observed isotopic shifts, as predominantly the C=O stretching vibration with a significant contribution from either the C–C stretching or CH$_2$ scissoring modes. The somewhat lower than anticipated [8] ^{18}O-shift is presumably the result of hydrogen bonding effects. The assignment of the high frequency shoulder at 1 610 cm^{-1}, the isotopic shifts of which are impossible to determine, to either the NH$_2$ or H$_2$O scissoring mode [5,12] cannot be distinguished in the present work.

The assignment [5] of the 1 411 cm^{-1} absorption as C–O stretching with C–C stretching appears to be correct. However, the assignment [5] of the neighbouring bands at 1 439 and 1 349 cm^{-1} to pure CH$_2$ scissoring and wagging

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modes respectively is incorrect. Although both these bands show the expected 2-^{13}C-shifts which justify their assignment to the CH_2 bending modes, they are significantly affected by ^{18}O- and 1-^{13}C-substitution to suggest coupling to the C–O stretch. The band at 1 324 cm^{-1} in the spectrum of α-glycine, which has been shown [13] to shift -10 cm^{-1} on ^{18}O-labelling, was assigned to CH_2 wagging + C–CO_2 stretching. A similar assignment is not made here because a significant contribution from the C–C stretching vibration would be expected to yield a larger 1-^{13}C-shift than is observed.

Band frequencies (cm^{-1}), ^{15}N-induced shifts (Δν^{15}N),[a] ^{18}O-induced shifts (Δν^{18}O),[a] 1-^{13}C-induced shifts (Δν1-^{13}C),[a] 2-^{13}C-induced shifts (Δν2-^{13}C),[a] and assignments in the i.r. spectrum of *trans*-[$Ni(gly)_2(H_2O)_2$] (all other shifts above 600 cm^{-1} <1.5 cm^{-1} and below 600 cm^{-1} <1 cm^{-1})

ν	Δν^{15}N	Δν^{18}O	Δν1-^{13}C	Δν2-^{13}C	Assignments
3 328	5				N–H asym. stretch
3 272	4				N–H symm. stretch
3 190br					O–H stretch
2 977				9	C–H asym. stretch
2 937				8	C–H symm. stretch
1 610sh					NH_2 or OH_2 scissor
1 590	2	18	33	5	C=O stretch
1 439		6	8	4	CH_2 scissor + C–O stretch
1 411		21	22	6	C–O stretch + C–C stretch
1 349		9.5	9	5.5	CH_2 wag + C–O stretch
1 305	3	2	1.5	4.5	CH_2 wag + NH_2 twist
1 185			4	3.5	CH_2 twist + C–C stretch
1 096	3	2			NH_2 wag
1 042	15.5	2		18	C–N stretch
950		12.5	5	6.5	CO_2 scissor + C–C stretch
916		35	6	7	CO_2 scissor + CH_2 rock
790br					OH_2 rock
738	2	24	4	4.5	CO_2 rock + CH_2 rock + NH_2 rock
676	2.5				NH_2 rock
626					OH_2 rock
596	2	11	6	2	CO_2 wag + ring deformation
518	2	10.5	2		CO_2 wag + Ni–N stretch
437	6 [b]	5			Ni–N stretch + Ni–O stretch
334		5			Ni–O stretch
283		3			O–Ni–O bend
227					OH_2 libration or H-bond stretch
202					
187	2	5.5			N–Ni–O bend
150					OH_2 libration or H-bond stretch

[a] All shifts are to lower wavenumber. [b] Doublet, 438 and 431 cm^{-1}.

The 1 305 cm^{-1} band, not mentioned in the normal co-ordinate analysis,[5] is assigned to the CH_2 wagging + NH_2 twisting modes by virtue of the ^{15}N- and 2-^{13}C-isotopic shifts. Slight coupling of the C–O stretch is evident from the smaller ^{18}O- and 1-^{13}C-shifts. The CH_2 twisting vibration [5] at 1 185 cm^{-1} shows coupling to the C–C stretch. The ^{13}C-shifts of this absorption are, however, too small to suggest any major contribution from the C–C stretch.

The previous assignment [5] of the band at 1 096 cm^{-1} to the NH_2 wagging, NH_2 twisting, and C–N stretching modes appears to require revision since it is totally insensitive to 2-^{13}C-substitution. Its assignment to the NH_2 wagging mode is therefore suggested in view of the assignment of the NH_2 twist at 1 305 cm^{-1}. The large ^{15}N- and 2-^{13}C-shifts of the 1 042 cm^{-1} absorption strongly support its assignment to the C–N stretch vibration. The earlier assignment [5] of this band to predominantly the NH_2 wag must therefore be discarded.

The CH_2 rocking and C–C stretching vibrations have previously been assigned [5] at 916 and 950 cm^{-1} respectively. The significant ^{18}O-sensitivity of the 916 cm^{-1} absorption suggests its assignment as the CO_2 scissoring vibration. The smaller 1-^{13}C-shift is consistent with this mode. Coupling to the CH_2 rock is apparent from the 2-^{13}C-sensitivity. The higher frequency band at 950 cm^{-1} which shows a much reduced ^{18}O-shift relative to that observed for the 916 cm^{-1} band, while both the 1- and 2-^{13}C-shifts remain of the order of -6 cm^{-1}, is assigned to the C–C stretch coupled to the CO_2 scissoring mode. It is noteworthy that because of the relatively small 2-^{13}C-shifts no one band in the spectrum of this complex may be assigned as predominantly the C–C stretch. ^{13}C-Shifts of the order of -15 cm^{-1} would be expected [8] for this vibration.

The isotopic shifts of the broad absorption at 790 cm^{-1} cannot be determined with any degree of accuracy. The fact that this band disappears on dehydration of the complex supports its assignment to the H_2O wagging vibration. All forms of isotopic substitution shift the 738 cm^{-1} band, however, because of the magnitudes of the ^{18}O- and 1-^{13}C-shifts it is assigned primarily to the CO_2 rocking vibration. The accompanying ^{15}N- and 2-^{13}C-shifts infer coupling to the CH_2 and NH_2 rocking modes. The band at 676 cm^{-1}, that was not assigned in the normal co-ordinate treatment,[5] is assigned to the NH_2 rocking vibration. Previously, the isotopically

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insensitive band at 626 cm^{-1} was assigned [4,5] as the NH_2 wag. We have reassigned this band to the H_2O wagging mode. Since both the 676 and 626 cm^{-1} absorptions disappear on dehydration, it appears that the NH_2 rock is moved under neighbouring bands in the anhydrous complex.

By virtue of the ^{18}O-shift of the 596 cm^{-1} band it is assigned to the CO_2 wag. The larger than expected 1-^{13}C-shift (relative to that observed for the CO_2 scissoring mode) and the ^{15}N- and 2-^{13}C-shifts of this band indicate coupling of the CO_2 wag to a ring deformation mode previously assigned [5] near 520 cm^{-1}. This latter band is assigned here to CO_2 wagging + Ni–N stretching, the relative magnitudes of the ^{18}O- and 1-^{13}C-shifts being consistent with its assignment [4,5] to CO_2 bending while the absence of 2-^{13}C-sensitivity rules out a contribution from a ring deformation mode. The position of this band and the ^{15}N-sensitivity thus infer a contribution from the Ni–N stretch.

The weak absorption at 437 cm^{-1} is sensitive to ^{15}N- and ^{18}O-substitution and is therefore assigned as Ni–N + Ni–O(gly) stretching. Vibrational mixing of the metal–ligand stretches is therefore evident. Nakamoto *et al.*[5] assigned this band to Ni–N stretching while Lane *et al.*[4] did not report it in their study.

The assignments by Lane *et al.*[4] of the absorption at 334 cm^{-1} to CCN bending was supported by the occurrence of a band in this region in the spectrum of glycine. Nakamoto *et al.*[5] assigned it as one of the out-of-plane ring deformation modes which had not been calculated in their normal co-ordinate treatment. The absence of ^{15}N- and ^{13}C-sensitivity of this band establishes that both these assignments are incorrect and demonstrates the danger of making assignments by comparison of the spectrum of the ligand with that of the complex. We assign this band to the Ni–O(gly) stretching vibration. The ^{18}O-shift of -3 cm^{-1} observed for the 283 cm^{-1} band clearly shows that it is not due to the Ni–N stretch as calculated by Lane *et al.*[4] or to a Ni–O(gly) stretch with a contribution from the Ni–N stretch as claimed by Nakamoto *et al.*[5] It is possible that the small shift of -3 cm^{-1} may be the result of mixing of the Ni–O(gly) and Ni–OH_2 stretches. Alternatively, the assignment of this band to an O–Ni–O bending mode would be consistent with a similar assignment of an ^{18}O-sensitive band in this position in the spectrum of *cis*-$[Cu(gly)_2(H_2O)]$.[14] In that work [14] the assignment was supported by the fact that such a vibration would not involve appreciable movement of the Cu atom and thus account for its insensitivity [15] to ^{63}Cu–^{65}Cu substitution. On the basis of its position and its ^{15}N- and ^{18}O-shifts, the band at 187 cm^{-1} is assigned as a N–Ni–O(gly) bending mode.

It is of interest to note that all the bands assigned as having metal–ligand character in the spectrum of *trans*-$[Ni(gly)_2(H_2O)_2]$ occur at a lower wavenumber than those [7] for the corresponding Cu^{II} complex. This order, Cu > Ni, is associated with the higher crystal field stabilization energy of Cu^{II} relative to that of Ni^{II} and has been found to pertain to the metal–ligand bands of numerous complexes.[16]

The remaining bands at 227, 202, and 150 cm^{-1} which are not moved by isotopic substitution are probably associated with H_2O librational modes or hydrogen bond stretches which would be expected to yield very small ^{15}N- or ^{18}O-shifts.

Normal co-ordinate treatments have been performed on complexes of isoleucine,[17] valine,[18] leucine,[19] alanine,[20] serine,[21] and phenylalanine.[22] However, band assignments of the metal–ligand stretching vibrations for these complexes were initially based on these authors' incorrect assignments for the glycine complexes.[4,7] Subsequent treatment, *e.g.*, in the case of complexes of phenylalanine,[22] were based on results obtained for complexes of glycine,[4,7] valine,[18] leucine,[19] and alanine.[20] Erroneous assignments and invalid conclusions drawn in respect to the force constants of the metal–ligand bonds, on the basis of their exact stretching frequencies, have thus permeated their way through several normal co-ordinate treatments.[17-22] The results of the present study support the contention [9] that normal co-ordinate treatments are unreliable as solutions to the problem of band assignments in the i.r. spectra of metal complexes.

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