

Band Assignments in the Infrared Spectrum of Cadmium Glycinate Monohydrate by Multiple Isotopic Labelling

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The infrared spectra of the complex $[\text{Cd}(\text{glycinate})_2] \cdot \text{H}_2\text{O}$ and its ^{18}O -, ^{15}N -, $1\text{-}^{13}\text{C}$ -, $2\text{-}^{13}\text{C}$ -, $2,2\text{-d}_2$ and N,N-d_2 -labelled analogues have been determined over the range $4000\text{--}140\text{ cm}^{-1}$. Each band in the spectrum has been assigned on the basis of the shifts induced by the various modes of isotopic labelling. The C–H, C=O, C–C and C–N stretching vibrations and the NH_2 scissoring and rocking modes are vibrationally pure but all other bands, including the metal–ligand modes, exhibit vibrational coupling.

Introduction

Isotopic labelling of ligand atoms has been usefully employed [1] in yielding reliable assignments for the infrared bands of metal complexes including those of amino acids [2, 3]. The diatomic molecule relationship:

$$\nu^1/\nu = (\mu/\mu^1)^{1/2}$$

(where ν and ν^1 are the vibrational frequencies for the normal and labelled species and μ and μ^1 are their respective reduced masses) yields reliable values for the expected isotopically-induced shifts on labelling one atom of a diatomic species even in polyatomic molecules. Where the observed shifts are significantly smaller than predicted, special effects may safely be assumed to operate [1]. Of relevance to amino acid complexes, such effects include vibrational coupling and hydrogen bonding.

In this paper, which is the first to report assignments based on the independent isotopic substitution of every ligand atom in an amino acid complex, the spectrum of $[\text{Cd}(\text{gly})_2] \cdot \text{H}_2\text{O}$ (gly = glycinate anion) is discussed. A crystallographic study of the complex [4] has revealed slightly distorted octahedral coordination in which two glycinate ligands chelate with the metal ion in a *trans*-planar array while the axial positions are occupied by the carboxyl oxygen atoms of neighbouring glycinate ligands (Figure 1). There is extensive hydrogen bonding between the amino groups, neighbouring carbonyl oxygen atoms and the water molecule which is uncoordinated.

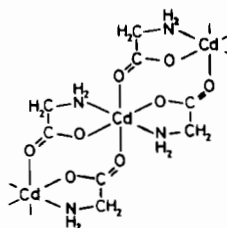


Figure 1. Diagram showing co-ordination of glycinate ligands to Cd^{2+} in $[\text{Cd}(\text{gly})_2] \cdot \text{H}_2\text{O}$.

Results and Discussion

The spectra of $[\text{Cd}(\text{gly})_2] \cdot \text{H}_2\text{O}$ and its isotopically-substituted analogues are depicted in Figure 2 while the frequencies and shifts ($\Delta\nu$) are recorded in Table I.

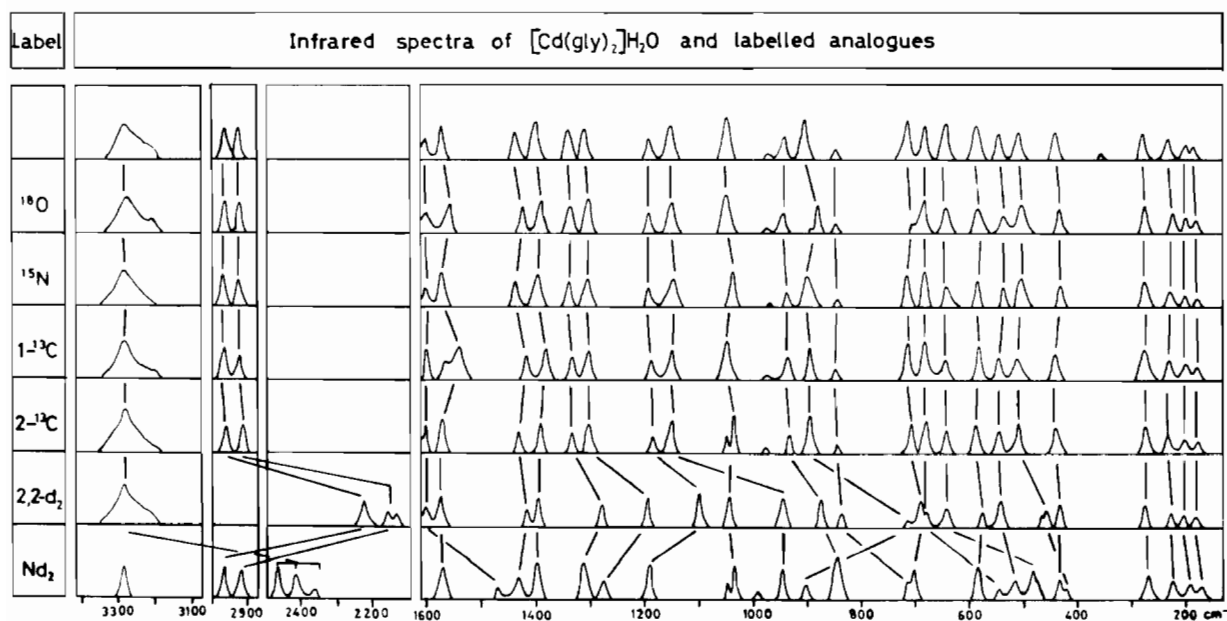
Hydrogen bonding causes the $\nu(\text{N-H})$ and $\nu(\text{O-H})$ bands to occur in the same spectral region, leading to a broad, unresolved band centred at 3280 cm^{-1} . Small differences in the frequency of the main peak indicate that, in certain of the complexes, the $\nu(\text{N-H})$ bands are more intense than the $\nu(\text{O-H})$ bands, while in others, the reverse is true. However, the $\nu(\text{N-H})$ assignment is supported by a 7 cm^{-1} shift on ^{15}N -labelling and confirmed by the appearance of new bands at 2473 , 2420 and 2368 cm^{-1} on N,N-d_2 labelling, leaving a relatively sharp band in the 3280 cm^{-1} region. This feature suggests that deuteration of the amino group does not simultaneously exchange deuterium oxide for the lattice water or that re-exchange with atmospheric water had occurred.

The $2\text{-}^{13}\text{C}$ - and $2,2\text{-d}_2$ -sensitivities of the bands at 2973 and 2929 cm^{-1} permits the assignment of these bands to the antisymmetric and symmetric $\nu(\text{C-H})$ modes. The magnitudes of the shifts which occur on both types of isotopic substitution are close to those predicted by the diatomic molecule relationship. This observation, and the insensitivity of these bands towards other forms of isotopic labelling, implies that these modes are vibrationally pure. The band at 1609 cm^{-1} is the vibrationally pure NH_2 scissoring mode since it is shifted only by ^{15}N - and N,N-d_2 -labelling.

TABLE I. Frequencies, Isotopically-induced Shifts and Infrared Band Assignments for $[\text{Cd}(\text{gly})_2] \cdot \text{H}_2\text{O}$ (cm^{-1})^a.

| ν | $\Delta\nu$ | | | | | | Assignments |
|-------|-----------------|-----------------|--------------------|--------------------|--------------------|--------------------|--|
| | ¹⁸ O | ¹⁵ N | 1- ¹³ C | 2- ¹³ C | 2,2-d ₂ | N,N-d ₂ | |
| 3280 | | 7 | | | | ~850 | $\nu(\text{N-H}) + \nu(\text{O-H})$ |
| 2973 | | | | 11 | 743 | | $\nu(\text{C-H})_{\text{as}}$ |
| 2929 | | | | 8 | 769 | | $\nu(\text{C-H})_{\text{s}}$ |
| 1609 | | 2 | | | | 134 | NH ₂ scissor |
| 1574 | 10 | | 40 ^b | | | 1 | $\nu(\text{C=O})$ |
| 1438 | 7 | | 12 | 3 | 10 | | $\nu(\text{C-O}) + \text{CH}_2$ scissor |
| 1401 | 3 | | 15 | 5 | | | $\nu(\text{C-O}) + \nu(\text{C-C})$ |
| 1344 | 4 | 2 | 4 | 4 | 60 | 20 | $\nu(\text{C-O}) + \text{CH}_2$ wag + NH ₂ twist |
| 1316 | 5 | 1 | 3 | 6 | 119 | 43 | |
| 1198 | | | 5 | 5 | 95 | | $\nu(\text{C-C})$ |
| 1155 | | 2 | | 3 | 207 | 200 | CH ₂ twist + NH ₂ wag |
| 1058 | | 13 | | 18 | 10 | 17 | $\nu(\text{C-N})$ |
| 947 | | 1 | 9 | 8 | 69 | 96 | $\nu(\text{C-C}) + \text{CH}_2$ twist + NH ₂ wag |
| 907 | 26 | | 6 | 7 | 180 | | CO ₂ scissor + CH ₂ rock |
| 857 | | 1 | | | 20 | 139 | NH ₂ rock |
| 723 | 18 | | 2 | 9 | 26 | 11 | CO ₂ rock + CH ₂ rock |
| 687 | | 1 | | | | 128 | NH ₂ rock |
| 646 | | 1 | | | | 155 | |
| 593 | 4 | | 5 | 1 | 15 | 4 | CO ₂ wag + ring def. |
| 552 | 8 | 6 | | | 6 | 30 | $\nu(\text{Cd-O}) + \nu(\text{Cd-N})$ |
| 514 | 8 | 3 | 2 | 1 | 52 | 93 | ring def. + $\nu(\text{Cd-O})$ |
| 443 | 8 | 6 | | | 7 | 9 | $\nu(\text{Cd-O}) + \nu(\text{Cd-N})$ |
| 280 | 5 | 2 | | | 2 | 4 | $\delta(\text{L-Cd-L})$ |
| 234 | 6 | 2 | | | 1 | 4 | |
| 204 | | 1 | | | 2 | 8 | |
| 186 | 3 | 3 | 3 | | 4 | 9 | |

^aAll shifts are to lower wavenumber. Absence of data implies shift $< 1 \text{ cm}^{-1}$. ^bWhen this shift occurs, a band at 1567 cm^{-1} is revealed in the spectrum of the 1-¹³C-labelled complex.

Figure 2. The infrared spectra of $[\text{Cd}(\text{gly})_2] \cdot \text{H}_2\text{O}$ and its labelled analogues.

The fact that the shifts are smaller than those calculated for the diatomic species is ascribed to hydrogen bonding effects. The band at 1574 cm^{-1} is uniquely sensitive to ^{18}O - and $1\text{-}^{13}\text{C}$ -labelling, suggesting its assignment to $\nu(\text{C}=\text{O})$. Again, hydrogen bonding causes an ^{18}O -shift which is smaller than the theoretical shift while the $1\text{-}^{13}\text{C}$ -shift is of the calculated order of magnitude for a vibrationally-pure $\nu(\text{C}=\text{O})$ band. Of all the modes of isotopic labelling employed, only $1\text{-}^{13}\text{C}$ -labelling shifts this band sufficiently to reveal an additional band at 1569 cm^{-1} which is assigned to the $\delta(\text{H}-\text{O}-\text{H})$ mode of the lattice water. In *trans*- $[\text{Ni}(\text{gly})_2(\text{H}_2\text{O})_2]$, in which the H_2O molecules are coordinated, the analogous band occurs [3] at 1610 cm^{-1} .

On the grounds of their sensitivities towards ^{18}O -, $1\text{-}^{13}\text{C}$ -, $2\text{-}^{13}\text{C}$ - and $2,2\text{-d}_2$ -labelling, the bands at 1438 and 1401 cm^{-1} are assigned to the coupled vibrations, $\nu(\text{C}-\text{O}) + \text{CH}_2$ scissor and $\nu(\text{C}-\text{O}) + \nu(\text{C}-\text{C})$, respectively. The small $2,2\text{-d}_2$ -shift compared with that observed for the vibrationally-pure CH_2 scissoring mode in $[\text{Ni}(\text{gly})_2(\text{H}_2\text{O})_2]$ is consistent with the coupled nature of the vibration in the cadmium complex. That multiple coupling occurs in the bands within the range $1300\text{--}1400\text{ cm}^{-1}$ is implied by their sensitivities towards all modes of labelling. The assignments proposed are those most reasonably indicated by the nature of the shifts and the region in which the bands occur.

The band at 1198 cm^{-1} is firmly assigned to $\nu(\text{C}-\text{C})$ on the grounds of the equivalent shifts observed for ^{13}C -labelling of both carbon atoms and the substantial shift which occurs on $2,2\text{-d}_2$ substitution. The $\nu(\text{C}-\text{N})$ band occurs at 1058 cm^{-1} . The ^{15}N - and $2\text{-}^{13}\text{C}$ -shifts are close to the theoretical values, implying that the band is vibrationally pure. Assignment of the coupled vibrations within the $500\text{--}1000\text{ cm}^{-1}$ region follows logically from the observed isotopic shifts and by analogy with earlier assignments [2, 3] in glycinate complexes.

The band at 857 cm^{-1} is assigned to the NH_2 rocking mode by virtue of its sensitivity to ^{15}N - and N,N-d_2 labelling. The observed $2,2\text{-d}_2$ shift may originate from an accidental degeneracy of the NH_2 rock with the coupled band, $\nu(\text{C}-\text{C}) + \text{CH}_2$ twist + NH_2 wag, which occurs at 878 cm^{-1} in the $2,2\text{-d}_2$ labelled complex. Bands at 687 and 646 cm^{-1} which are only sensitive to ^{15}N - and N,N-d_2 labelling, are also assigned to NH_2 rocking modes. The 646 cm^{-1} band probably corresponds with the 626 cm^{-1} band in $[\text{Ni}(\text{gly})_2(\text{H}_2\text{O})]$ where it was assigned [3] to an OH_2 rock. Had that study included N,N-d_2 labelling, it is possible that a shift would have been observed and have led to its assignment to an NH_2 rock.

The bands at 552 and 443 cm^{-1} are particularly sensitive to ^{15}N - and ^{18}O -labelling. They are assigned to coupled $\nu(\text{Cd}-\text{O})$ and $\nu(\text{Cd}-\text{N})$ modes. No bands in this region are uniquely sensitive to only ^{18}O - or only

^{15}N -labelling. Hence, there are no vibrationally pure $\nu(\text{Cd}-\text{O})$ or $\nu(\text{Cd}-\text{N})$ bands. The relatively high frequencies of these metal-ligand modes suggests that there is considerable covalency in both the $\text{Cd}-\text{O}$ and $\text{Cd}-\text{N}$ bonds. This contradicts an earlier suggestion [5] that the $\text{Cd}-\text{O}$ bonds are ionic, a suggestion which is also contrary to the crystallographically-determined [4] $\text{Cd}-\text{O}$ bond lengths in $[\text{Cd}(\text{gly})_2] \cdot \text{H}_2\text{O}$.

Bands below 300 cm^{-1} also exhibit sensitivity to both ^{15}N - and ^{18}O -labelling suggesting their assignment to coupled Cd -ligand bending modes.

Experimental

The complexes were prepared by the method reported [4] for $[\text{Cd}(\text{gly})_2] \cdot \text{H}_2\text{O}$. Except for the N,N-d_2 -labelled complex (which was prepared by dissolving the unlabelled complex in D_2O and allowing crystallization to occur under reduced pressure) the remaining labelled complexes were synthesized from commercial samples of the isotopically-substituted ligands (% isotopic purity in parentheses): glycine- $^{18}\text{O}_2$ (74%), glycine- ^{15}N (95%), glycine- $1\text{-}^{13}\text{C}$ (90%) and glycine- $2\text{-}^{13}\text{C}$ (91%) supplied by BOC Prochem Ltd. and glycine- $2,2\text{-d}_2$ (98%) supplied by Merck, Sharp and Dohme (Canada) Ltd. Purity of the complexes was established by microanalysis. Calcd. for $[\text{Cd}(\text{gly})_2] \cdot \text{H}_2\text{O}$: 17.25% C, 3.62% H, 10.06% N. Found for unlabelled complex: 17.35% C, 3.65% H, 10.05% N. Found for ^{18}O -labelled complex: 17.35% C, 3.65% H, 10.00% N. Found for ^{15}N -labelled complex: 17.25% C, 3.60% H, 10.05% N. Found for $1\text{-}^{13}\text{C}$ -labelled complex: 17.35% C, 3.65% H, 10.15% N. Found for $2\text{-}^{13}\text{C}$ -labelled complex: 17.20% C, 3.55% H, 10.05% N. Found for $2,2\text{-d}_2$ -labelled complex: 17.35% C, 3.65% H, 10.00% N.

Infrared spectra were determined on nujol mulls (or hexachlorobutadiene mulls in the region of nujol absorption) between caesium iodide plates on a Beckman IR-12 spectrophotometer ($4000\text{--}250\text{ cm}^{-1}$) and between polyethylene plates on a Perkin-Elmer 180 spectrophotometer ($250\text{--}140\text{ cm}^{-1}$). The reproducibility of reported frequencies is better than 0.5 cm^{-1} above 250 cm^{-1} and better than 1 cm^{-1} below 250 cm^{-1} .

Acknowledgements

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References

- 1 S. Pinchas and I. Lulicht, "*Infrared Spectra of Labelled Compounds*", Academic Press, New York (1971).
- 2 G. C. Percy, *Spectrochim. Acta*, *32A*, 1287 (1976).
- 3 G. C. Percy and H. S. Stenton, *J. Chem. Soc. Dalton Trans.*, 1466 (1976).
- 4 B. W. Low, F. L. Hirshfeld and F. M. Richards, *J. Am. Chem. Soc.*, *81*, 4412 (1959).
- 5 D. M. Sweeny, C. Curran and J. V. Quagliano, *J. Am. Chem. Soc.*, *77*, 5508 (1955).