

# Vibrations of the Water Molecules in the Crystalline Monohydrates of *cis*- and *trans*-Bis(glycinato)copper(II) and *trans*-Bis(DL- $\alpha$ -alaninato)copper(II)

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Internal vibrations and librations of the water molecules in *cis*- and *trans*-bis(glycinato)copper(II) monohydrate,  $\text{Cu}(\text{NH}_2\text{CH}_2\text{CO}_2)_2 \cdot \text{H}_2\text{O}$ , and *trans*-bis(DL- $\alpha$ -alaninato)copper(II) monohydrate,  $\text{Cu}\{\text{NH}_2\text{CH}(\text{CH}_3)\text{CO}_2\}_2 \cdot \text{H}_2\text{O}$ , have been assigned from the infrared spectra of powder samples at temperatures between 100 K and 300 K. D and <sup>18</sup>O substitution were used to distinguish the vibrations localized to the water molecule from other vibrations.

The ability of metal cations, in particular transition metal cations, to form strong complexes with ligand molecules or anions, plays an important role in many biological processes. For that reason, complexes between metal cations and amino acids have been extensively studied, both in aqueous solution and in the crystalline state (see e.g. a recent review article by Hay and Nolan<sup>1</sup>).

As regards crystals, vibrational spectroscopy has been used to obtain information about the structure of metal ion – amino acid complexes and about the strength of the interaction between the components of the complexes. These studies usually involve conventional IR or Raman spectroscopy on powder samples at room temperature; sometimes isotopic substitution has been used. In some cases, normal coordinate and force constant calculations have been included in the study.

In this paper, we discuss the vibrations of the water molecule in three compounds: *cis*- and *trans*-bis(glycinato)copper(II) monohydrate,  $\text{Cu}(\text{NH}_2\text{CH}_2\text{CO}_2)_2 \cdot \text{H}_2\text{O}$ , and *trans*-bis(DL- $\alpha$ -alaninato)copper(II) monohydrate,  $\text{Cu}\{\text{NH}_2\text{CH}(\text{CH}_3)\text{CO}_2\}_2 \cdot \text{H}_2\text{O}$  (in the following written as *cis*- and *trans*- $\text{Cu}(\text{gly})_2 \cdot \text{H}_2\text{O}$  and  $\text{Cu}(\text{DL-ala})_2 \cdot \text{H}_2\text{O}$ , respectively). In earlier spectroscopic studies of these compounds,<sup>2–11</sup> very little attention has

been paid to the details of the vibrations of the water molecules.

We have studied the infrared spectra of powdered samples at temperatures between 100 K and 300 K and we have used isotopic substitution to determine wavenumbers for the internal vibrations and librations of the water molecules. We discuss our results in relation to existing knowledge concerning the vibrations of water molecules in crystals.

The results reported here are part of an extensive study of metal ion – amino acid complexes by infrared spectroscopy.<sup>12</sup> Some results concerning the vibrations of the water molecule in  $\text{Cu}(\text{DL-ala})_2 \cdot \text{H}_2\text{O}$  have been published earlier.<sup>13</sup>

## Crystal structures

In the cases of *cis*- $\text{Cu}(\text{gly})_2 \cdot \text{H}_2\text{O}$  and  $\text{Cu}(\text{DL-ala})_2 \cdot \text{H}_2\text{O}$ , the crystal structures have been determined by X-ray diffraction measurements on single crystals.<sup>14,15</sup> In both cases, the copper ion is coordinated to two anions, each of which forms a bidentate ligand via its amino nitrogen atom and one of its carboxylate oxygen atoms (Cu-N distances 198–202 pm, Cu-O distances 194–195 pm). The copper ion and the four ligand donor atoms are approximately in the same plane.

For *cis*- $\text{Cu}(\text{gly})_2 \cdot \text{H}_2\text{O}$ , all the constituents of

the crystal occupy  $C_1$  sites. The copper ion is also coordinated to two other oxygen atoms at longer distances (240 pm for the water oxygen atom and 274 pm for a carboxylate oxygen atom). The water molecule acts as a hydrogen bond donor to carboxylate oxygen atoms ( $O\cdots O$  distances 276 and 280 pm). These two oxygen atoms together with the copper ion give the water molecule a trigonal environment of nearest neighbours.<sup>14</sup>

The copper ion of  $Cu(DL\text{-ala})_2 \cdot H_2O$  is at a centre of symmetry and is coordinated to, in addition to two alaninate ions, two crystallographically equivalent water molecules (Cu-O distance 268 pm). The water molecule is at a two-fold axis and is hydrogen-bonded to oxygen atoms of the carboxylate group ( $O\cdots O$  distance 276 pm). The coordination of the water molecule is tetrahedral since two copper ions are nearest neighbours to the water oxygen atom.<sup>15</sup>

The crystal structure of  $trans\text{-Cu(gly)}_2 \cdot H_2O$  has been studied by electron diffraction.<sup>16</sup> Again, the copper ion and the two glycinate ions form an approximately planar complex with two Cu-N and two Cu-O contacts (both types around 200 pm). In the directions perpendicular to this plane, two other glycinate ions are coordinated via carboxylate oxygen atoms (Cu-O distances around 280 pm). The water molecule is found to be "located outside the coordination sphere of the copper ion in channels formed between the copper glycinate molecules." However, the details are not clear since no positional coordinates or drawings of the structure were published.

The space groups suggested for  $cis\text{-}$  and  $trans\text{-Cu(gly)}_2 \cdot H_2O$  and for  $Cu(DL\text{-ala})_2 \cdot H_2O$  are  $P2_12_12_1$ ,  $C2/c$  and  $C2/c$ , respectively. The number of formula units per unit cell is 4 in all three cases.

General aspects on crystal structures of metal-peptide complexes can be found in an old, but still highly relevant article by Freeman.<sup>17</sup>

## Experimental

$Cis\text{-Cu(gly)}_2 \cdot H_2O$  was obtained from an aqueous solution of glycine and a readily soluble copper salt.<sup>11</sup> The product was recrystallized from water.  $trans\text{-Cu(gly)}_2 \cdot H_2O$ , the thermodynamically more stable form,<sup>10</sup> was obtained from  $cis\text{-Cu(gly)}_2 \cdot H_2O$  suspended in a saturated aqueous solution which was kept on a water bath for about 10 h at 80°C.<sup>10</sup>  $Cu(DL\text{-ala})_2 \cdot H_2O$  was prepared

from copper(II) hydroxide and DL-alanine following a method described by Segnini *et al.*<sup>18</sup>

The water content of the three compounds was checked by thermogravimetric analysis, which showed that one water molecule per copper atom is lost on heating to 130–140°C. The theoretical weight losses are 7.84, 7.84 and 6.99% for one water molecule of  $cis\text{-}$  and  $trans\text{-Cu(gly)}_2 \cdot H_2O$  and  $Cu(DL\text{-ala})_2 \cdot H_2O$ , respectively. The measured values were 7.80, 7.89 and 7.14%.

The purities of  $cis\text{-}$  and  $trans\text{-Cu(gly)}_2 \cdot H_2O$  were further checked by copper analysis using atomic absorption spectroscopy. A copper content of 28.0% by weight was found in both cases, to be compared to the calculated value of 27.7% for a monohydrate.

Delf *et al.*<sup>10</sup> have shown, contrary to some earlier reports, that the  $trans$  isomer is a monohydrate. They also investigated the transformations between the  $cis$  and  $trans$  isomers of  $Cu(gly)_2 \cdot H_2O$ .

For  $cis\text{-Cu(gly)}_2 \cdot H_2O$  and  $Cu(DL\text{-ala})_2 \cdot H_2O$ , products with various H/D molar ratios were prepared by recrystallization from an aqueous solution. In another method, the water molecules were exchanged via the vapour phase. This was done in a closed vessel in which the relevant dehydrated compound (obtained by heating) and an appropriate amount of liquid water were kept separated from each other. Under these conditions the monohydrates formed within 20 h as judged by weighing and from the IR spectra. The amino hydrogen atoms were also exchanged by this method. For practical reasons, the exchange via the vapour phase was particularly useful for  $trans\text{-Cu(gly)}_2 \cdot H_2O$  and for  $H_2^{18}O$  substitution.

The isotopic purities of the  $D_2O$  and  $H_2^{18}O$  water used were 99.98% and 97%, respectively.

For IR spectroscopic measurements the samples were prepared as mulls in nujol or fluorolube between windows of  $CaF_2$  or KRS-5. A Perkin-Elmer 580B IR spectrophotometer and a Perkin-Elmer 3500 data station were used to record the spectra. Low temperature spectra were obtained using an RIIC-VLT cryostat. The resolution was typically about  $3\text{ cm}^{-1}$ ; in certain cases  $1\text{ cm}^{-1}$  was tried instead, but no further information was gained. The accuracy of measured peak positions was  $\pm 1\text{ cm}^{-1}$  except for less well-defined bands.

To obtain an *in situ* check that water molecules were not lost during the sample preparation and measurements, the spectra of the three anhy-

drous compounds and their deuteriated analogues were recorded. The absence of certain absorption bands, typical for the anhydrous form of the compound studied, then served as the desired criterion when the spectra of the hydrates were scanned.

## Results and discussion

Survey spectra of the three compounds at 100 K are shown in Fig. 1. Detailed spectra in wavenumber regions discussed below are presented in Figs. 2–5. The measured wavenumbers and assignments for water molecule vibrations are given in Table 1. Other types of vibration are discussed in some detail in Ref. 12 (our measurements) and in Refs. 2–11. For convenience, we have listed also the wavenumbers of some vibrations localized to the amino group in Table 1.

*Water stretching vibrations.* For the three compounds studied, it is immediately clear that there is substantial overlap between bands from the water molecule and amino group stretching vi-

brations. The overtones of the bending vibrations are also expected in the same wavenumber region, possibly in Fermi resonance with stretching vibrations. Factor group splitting could further complicate the situation. Isotopic substitution of D for H could partially solve these problems, but since the shifts for  $\text{H}_2\text{O}$  and  $\text{NH}_2$  are about the same and since selective deuteration is not possible, the remaining difficulties are severe. Also, the behaviour of the absorption bands on temperature variation (including heating to form gradually the anhydrous compounds) is not decisive for assignment purposes, although this method has been used by some authors.<sup>19,20</sup> Instead,  $^{18}\text{O}$  substitution in the water molecule gives the desired band separation and by using about 5%  $\text{HD}^{18}\text{O}$  in the  $\text{H}_2^{18}\text{O}$  samples, the OD stretching vibrations of isotopically diluted HDO molecules can be distinguished from ND stretching vibrations of NHD groups (see Fig. 3). However, for  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  stretching vibrations, the problem of overlapping bands is still insurmountable in some cases (Table 1, Figs. 2–3).

The observed OH and OD stretching wave-

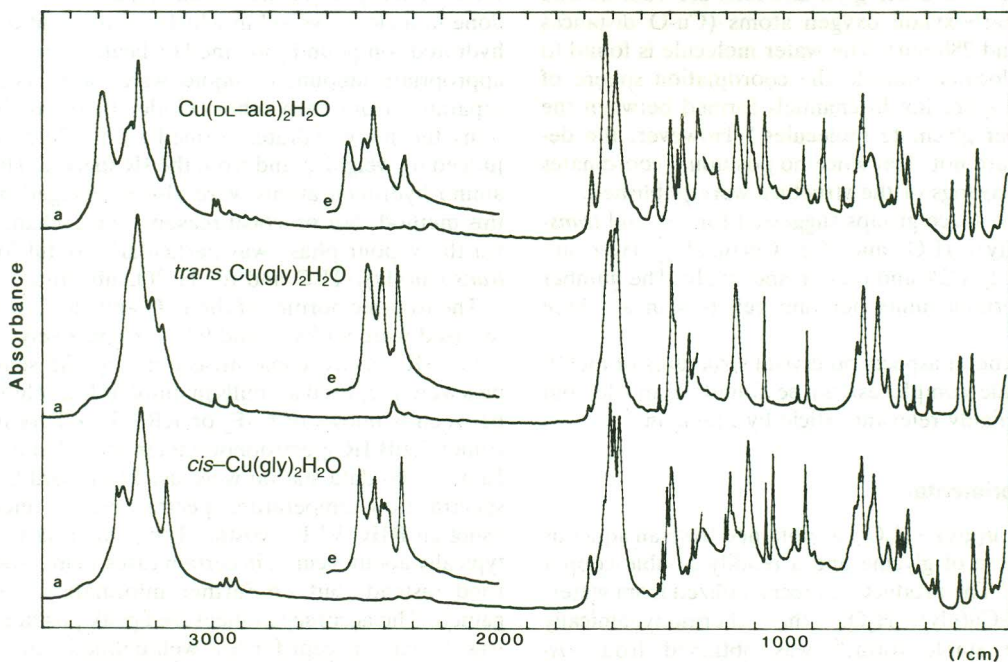


Fig. 1. Infrared spectra at 100 K of *cis*- $\text{Cu}(\text{gly})_2 \cdot \text{H}_2\text{O}$ , *trans*- $\text{Cu}(\text{gly})_2 \cdot \text{H}_2\text{O}$  and  $\text{Cu}(\text{DL-ala})_2 \cdot \text{H}_2\text{O}$  (denoted a) and their deuterated analogues (denoted e; H/D molar ratios around 0.1). The spectra are of samples in fluorolube mull ( $3600\text{--}1300\text{ cm}^{-1}$ ) and nujol mull ( $1300\text{--}200\text{ cm}^{-1}$ ; nujol peak around  $725\text{ cm}^{-1}$ ).

Table 1. Observed wavenumbers and assignments.<sup>a</sup>

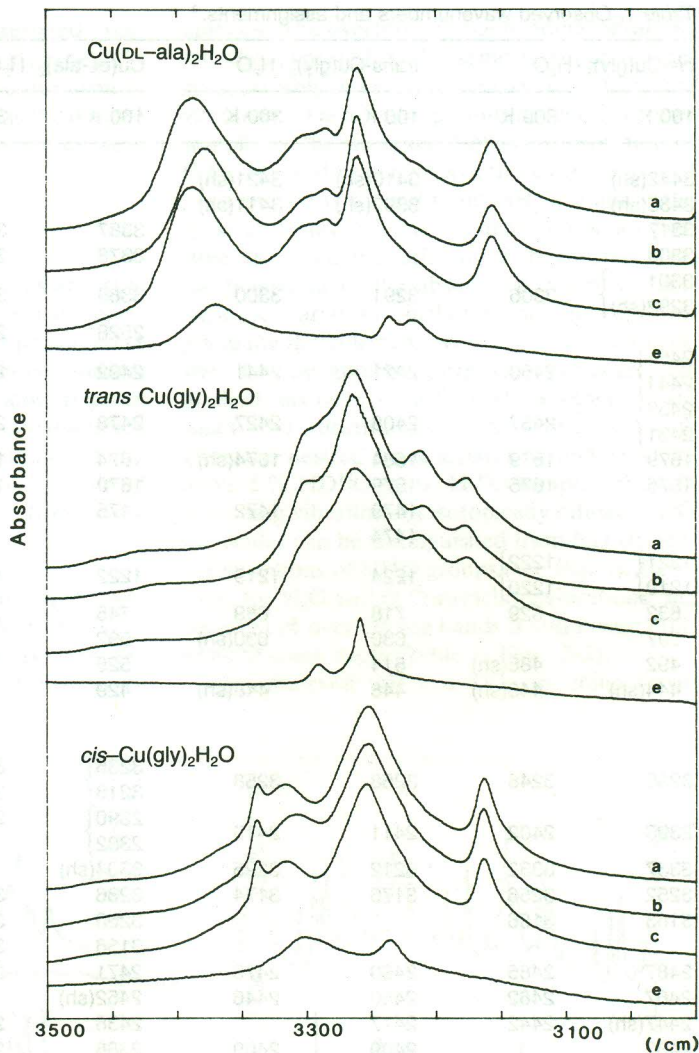
<i>cis</i> -Cu(gly) <sub>2</sub> · H <sub>2</sub> O		<i>trans</i> -Cu(gly) <sub>2</sub> · H <sub>2</sub> O		Cu(DL-ala) <sub>2</sub> · H <sub>2</sub> O		Assignment
100 K	300 K	100 K	300 K	100 K	300 K	
3442(sh)		3410(sh)	3421(sh)			$\nu(\text{H}_2\text{O}) + \text{T}(\text{H}_2\text{O})$
3435(sh)		3399(sh)	3411(sh)			$\nu(\text{H}_2^{18}\text{O}) + \text{T}(\text{H}_2^{18}\text{O})$
3317				3387	3389	$\nu_{\text{as}}(\text{H}_2\text{O})$
3308				3378	3380	$\nu_{\text{as}}(\text{H}_2^{18}\text{O})$
3301	3306	3291	3300	3369	3374	$\nu_{\text{OH}}(\text{HDO})$
3292(sh)}				2528	2534	$\nu_{\text{as}}(\text{D}_2\text{O})$
2451	2450	2421	2441	2492	2497	$\nu_{\text{OD}}(\text{HDO})$
2444				2478	2485	$\nu_{\text{OD}}(\text{HD}^{18}\text{O})$
2439						
2431	2437	2408	2427	2478	2485	$\nu_{\text{OD}}(\text{HD}^{18}\text{O})$
1679	1679	1684	1674(sh)	1674	1666	$\delta(\text{H}_2\text{O})$
1675	1675	1679		1670	1662	$\delta(\text{H}_2^{18}\text{O})$
		1479	1472	1475		$\delta(\text{HDO})$
		1474				$\delta(\text{HD}^{18}\text{O})$
1221	1222	1224	1219	1222	1218	$\delta(\text{D}_2\text{O})$
1219						
632	629	718	689	745	730	$\text{R}'(\text{H}_2\text{O})$
597		630	630(sh)	592	581(sh)	$\text{R}''(\text{H}_2\text{O})$
492	486(sh)	514		529	522(sh)	$\text{R}'(\text{D}_2\text{O})$
444(sh)	445(sh)	448	448(sh)	429	420	$\text{R}''(\text{D}_2\text{O})$
3235	3246	3258	3258	3236	3239	$\nu_{\text{NH}}(\text{NHD})$
				3218	3224	
2396	2402	2411	2413	2390	2393	$\nu_{\text{ND}}(\text{NHD})$
				2382		
3337	3332	3212	3225	3304(sh)		$\nu(\text{NH}_2)$ or $2\delta(\text{NH}_2)^b$
3252	3256	3176	3174	3286	3286(sh)	
3163	3156			3260	3265	
				3156	3156	
				2471	2469(sh)	
2487	2485	2460	2473	2471	2469(sh)	$\nu(\text{ND}_2)$ or $2\delta(\text{NH}_2)^b$
2467	2462	2450	2446	2452(sh)		
2447(sh)	2442	2417		2438	2443	
2433		2409	2409	2388	2396	
2409	2405	2372		2329	2334	
2397		2351	2354			
2385(sh)	2380					Rock (NH <sub>2</sub> )
2339	2340					
681	671	669	645	690	667	Rock (ND <sub>2</sub> )
521	513	497	490	485	472	

<sup>a</sup>Relative intensities are not given since it is difficult to compare spectra for varying isotopic compositions. <sup>b</sup>No detailed assignment is proposed.

numbers of isotopically diluted HDO molecules (Table 1) give  $\nu(\text{OH})/\nu(\text{OD})$  ratios of 1.35–1.36, in agreement with earlier findings for solid hydrates.<sup>21,22</sup> The wavenumbers (in the region 3370–3290  $\text{cm}^{-1}$  for OH and 2500–2430  $\text{cm}^{-1}$  for OD

stretching) correspond to medium strong hydrogen bonds. In particular, the values for *cis*-Cu(gly)<sub>2</sub> · H<sub>2</sub>O and Cu(DL-ala)<sub>2</sub> · H<sub>2</sub>O agree well with the O...O distances found in the structural investigations<sup>14,15</sup> (see Ref. 23, in which a correla-

Fig. 2. Infrared spectra at 100 K in the OH (and NH) stretching region of the three compounds in fluorolube mull. Spectra a, H<sub>2</sub>O samples; spectra b, samples containing approx. 95 % H<sub>2</sub><sup>18</sup>O + 5 % HD<sup>18</sup>O; spectra c, samples containing approx. 95 % H<sub>2</sub>O + 5 % HDO; e, samples with H/D molar ratios around 0.1. The intensities have been suitably scaled.



tion curve for OD stretching wavenumbers and O...O distances is published). For *trans*-Cu(gly)<sub>2</sub>·H<sub>2</sub>O and Cu(DL-ala)<sub>2</sub>·H<sub>2</sub>O, only one OH and OD band appear for HDO molecules. This implies that the OH (OD) bonds are equivalent within the resolution of the method [in agreement with the known crystal structure of Cu(DL-ala)<sub>2</sub>·H<sub>2</sub>O].

For H<sub>2</sub>O (and D<sub>2</sub>O) stretching vibrations, two vibrations are expected, possibly split by coupling to crystallographically equivalent water molecules and influenced by the bending overtone. Owing to the equivalence (or nearly so) of the

OH bonds (see above), these two vibrations should be well described as antisymmetric and symmetric stretching vibrations. According to Schiffer *et al.*,<sup>24</sup> the splitting between these two vibrations (if uncoupled) of H<sub>2</sub>O and D<sub>2</sub>O varies linearly with the OH(HDO) and OD(HDO) stretching wavenumbers, respectively. Accordingly, we assign bands sensitive to <sup>18</sup>O substitution and observed for *cis*-Cu(gly)<sub>2</sub>·H<sub>2</sub>O and Cu(DL-ala)<sub>2</sub>·H<sub>2</sub>O to the antisymmetric stretching vibration. The symmetric stretching vibrations are not observed but are expected<sup>24</sup> to have wavenumbers which are 20–30 cm<sup>-1</sup> (60–70 cm<sup>-1</sup> for

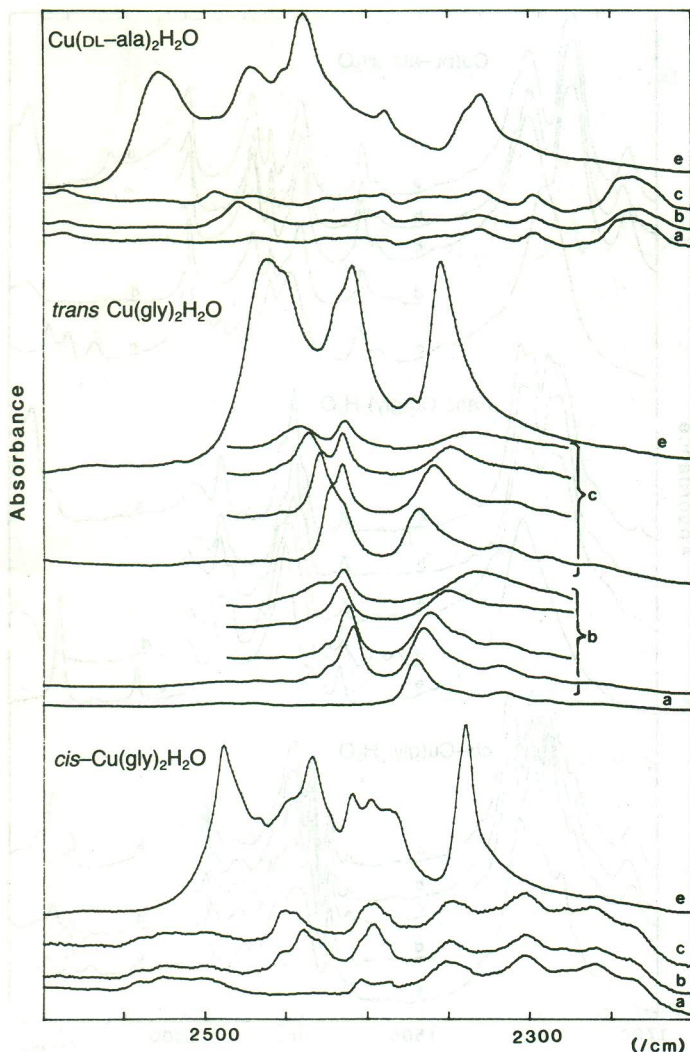


Fig. 3. Infrared spectra in the OD (and ND) stretching region of the three compounds in fluorolube mull. Notations as in Fig. 2. For *trans*-Cu(gly)<sub>2</sub>·H<sub>2</sub>O, the groups of spectra denoted b (4 spectra) and c (4 spectra) show the effect of temperature variation from 100 K (lower spectrum in each group) to 300 K (upper spectrum). All other spectra are for 100 K.

D<sub>2</sub>O) lower than for the antisymmetric stretching vibrations.

**Amino group stretching vibrations.** The wavenumbers found for isotopically diluted NHD groups (Table 1) suggest equivalent (or nearly so) NH bonds in *cis*- and *trans*-Cu(gly)<sub>2</sub>·H<sub>2</sub>O. In the former, the diffraction results show, in fact, four non-equivalent N–H bonds, three of which participate in relatively weak hydrogen bonds (N···O distances 298, 302 and 308 pm).<sup>14</sup>

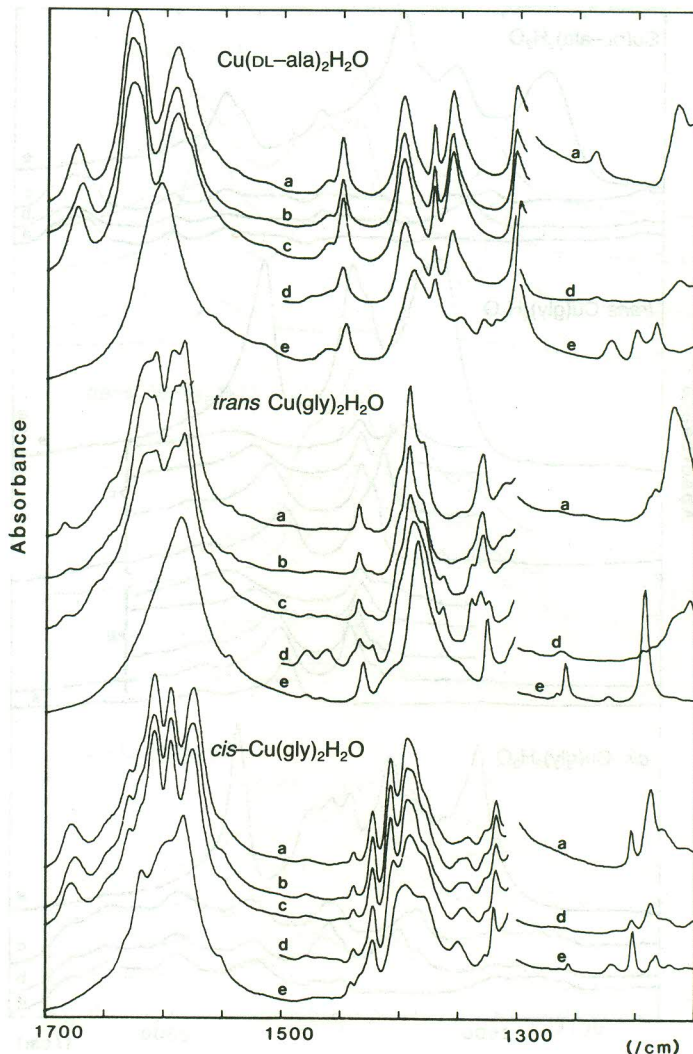
For Cu(DL-ala)<sub>2</sub>·H<sub>2</sub>O, the two observed wavenumbers for NHD groups imply at least two non-

equivalent N–H bonds, which is in agreement with the diffraction study (two N–H bonds; N···O distances 300 and 305 pm).<sup>15</sup>

All details concerning NH<sub>2</sub> vibrations in general are to be found in Ref. 12.

**Water bending vibrations.** In general, there are difficulties in locating the often weak band(s) due to H<sub>2</sub>O bending in the presence of the very strong bands around 1600 cm<sup>-1</sup> arising from NH<sub>2</sub> bending and COO stretching. Deuterium substitution shifts also the amino group bending vibration. Therefore, <sup>18</sup>O substitution in the water molecule

Fig. 4. Infrared spectra at 100 K in the water bending region (1700–1300  $\text{cm}^{-1}$ , fluorolube mulls; 1300–1150  $\text{cm}^{-1}$ , nujol mulls). Notation as in previous figs. In addition, the spectra denoted d are for samples containing approx. 25%  $\text{H}_2\text{O}$ , 50% HDO and 25%  $\text{D}_2\text{O}$ .



is again an important help. The theoretical shift for a pure  $\text{H}_2\text{O}$  bending vibration is, within the harmonic approximation, 5  $\text{cm}^{-1}$ . Shifts of this size are found for all three compounds for relatively weak bands in the region 1660–1685  $\text{cm}^{-1}$  (Table 1, Fig. 4). The corresponding  $\text{D}_2\text{O}$  bending vibrations are assigned to weak bands around 1200  $\text{cm}^{-1}$ . The  $\delta(\text{H}_2\text{O})/\delta(\text{D}_1\text{O})$  ratios obtained, 1.37–1.38, are in perfect agreement with theory and with results for other solid hydrates.<sup>21,25</sup>

In the case of HDO bending vibrations, a band can be assigned for *trans*- $\text{Cu}(\text{gly})_2 \cdot \text{H}_2\text{O}$  (Table 1, Fig. 4). This band, at 1479  $\text{cm}^{-1}$  (100 K), appears

together with a band at 1463  $\text{cm}^{-1}$ . The temperature shifts for these two bands are the same and the intensities vary in the same way with deuterium concentration. However, only the band at 1479  $\text{cm}^{-1}$  is sensitive to  $^{18}\text{O}$  substitution in the HDO molecule. For  $\text{Cu}(\text{DL-ala})_2 \cdot \text{H}_2\text{O}$ , a band (shoulder) at 1475  $\text{cm}^{-1}$  appears with notable intensity for samples with a D content of around 50% and is consequently assigned to bending of the HDO molecule. The wavenumber ratios,  $\delta(\text{H}_2\text{O})/\delta(\text{HDO})$ , for the cases discussed above are 1.13–1.14, again within the expected range,<sup>21,25</sup> thus giving support to the assignment.

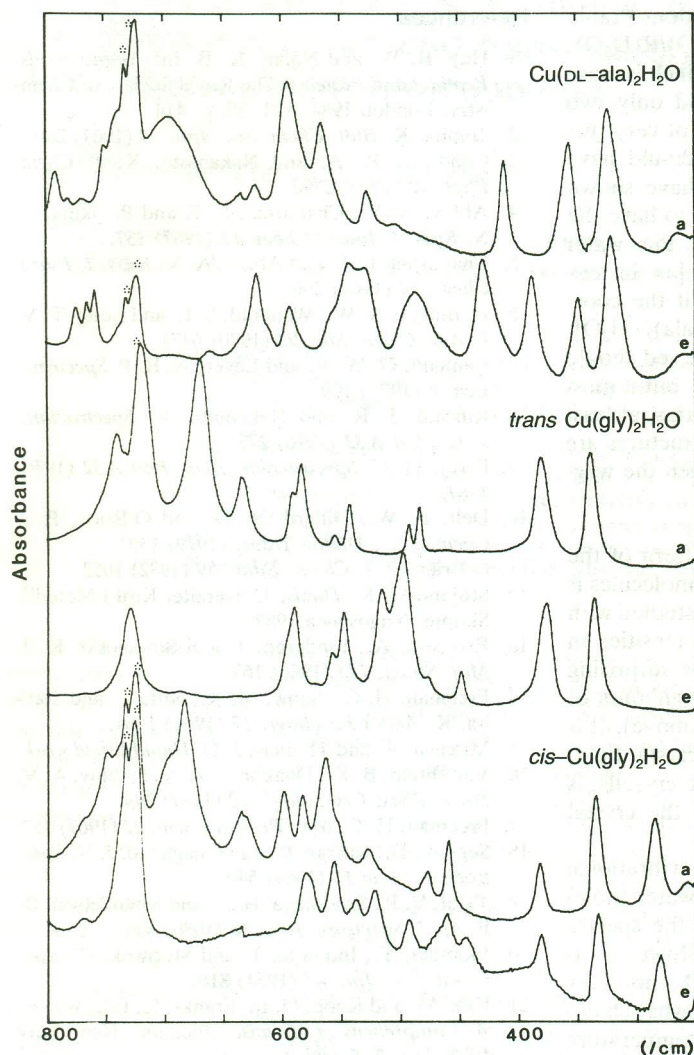


Fig. 5. Infrared spectra at 100 K in the water librational region (nujol mulls). Notation as in previous figs. The nujol band (subpeaks at 724 and 732  $\text{cm}^{-1}$ ) is marked with a star. Samples containing as little nujol as possible (at least 10 times lower relative content than for the spectra in this fig.) were also scanned to establish the spectral features in the region 750–700  $\text{cm}^{-1}$  (cf. Table 1).

**Water librations.** The assignment of the water librations presents an additional difficulty. The amino group rocking libration is expected in the same wavenumber region, and the two types of vibration cannot be distinguished by deuteration or by studying the temperature dependence of band positions and widths since similar behaviour is often observed. Substitution with  $^{18}\text{O}$  in the water molecule is expected to produce shifts of magnitude 0–3  $\text{cm}^{-1}$  for the librations, but, somewhat surprisingly, it was not possible to observe any shift at all within the experimental error.

For *cis*-<sup>8,9</sup> and *trans*- $\text{Cu(DL-ala)}_2 \cdot \text{H}_2\text{O}$ ,<sup>8</sup> the

$\text{NH}_2$  rocking libration was located following  $^{15}\text{N}$  substitution. This libration was also assigned on the basis of a normal coordinate analysis and spectra of four deuterium analogues of *cis*- $\text{Cu(gly)}_2 \cdot \text{H}_2\text{O}$ .<sup>3</sup> Herlinger *et al.*<sup>6</sup> have assigned the  $\text{NH}_2$  rocking libration for all three compounds on the basis of a Urey-Bradley force field analysis. Except for a proposed wagging libration in  $\text{Cu(DL-ala)}_2 \cdot \text{H}_2\text{O}$ ,<sup>6</sup> no water librational wavenumber has been reported in the literature.

The  $\text{NH}_2$  rocking librations have thus been identified and, taking these assignments as correct, we assign the other bands, sensitive to D

substitution, to water molecule librations (Table 1, Fig. 5). The isotopic ratios,  $R(\text{H}_2\text{O})/R(\text{D}_2\text{O})$ , have values in the range 1.28–1.40 which is close to what is expected. We have found only two bands for each compound, which is not very surprising; the twisting-type libration should have low intensity. Model calculations<sup>26</sup> have shown that the rocking libration is expected to have the highest librational wavenumber if the water molecule coordination is trigonal [as in  $\text{cis-Cu}(\text{gly})_2 \cdot \text{H}_2\text{O}$ ] and the lowest one if the coordination is tetrahedral [as in  $\text{Cu}(\text{DL-ala})_2 \cdot \text{H}_2\text{O}$ ]. The remaining librational band observed should then correspond to the wagging type, but it must be kept in mind that the site symmetries, at least in the two cases where the crystal structures are well established, allow mixing between the wagging and rocking librations.

**Concluding remarks.** The overall pattern of the vibrational bands arising from water molecules is very similar for the three compounds studied with regard to both wavenumbers and intensities in the infrared spectra. This is perhaps surprising since the environment of nearest neighbours of the water molecules is different (see above). It is tempting to suggest that the overall crystal field, determined by the constituents of the crystals, is more important than the details of the crystal structures.

Reports of earlier studies using vibrational spectroscopy<sup>2–11</sup> have discussed the water molecule vibrations very little, although the spectra must be expected to be influenced. However, as has been demonstrated in this work, not very much can be concluded without somewhat elaborate isotopic substitutions and low temperature studies.

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