

INFRARED SPECTRUM OF TRANS-BIS(DL- α -ALANINATO) COPPER(II)
MONOHYDRATE - STRETCHING AND BENDING VIBRATIONS OF THE WATER
MOLECULE AND THE AMINO GROUP

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ABSTRACT

The stretching and bending vibrations of the water molecule and the amino group in trans-bis(DL- α -alaninato) copper(II) monohydrate, $(\text{NH}_2\text{CH}(\text{CH}_3)\text{COO})_2\text{Cu}(\text{II})\cdot\text{H}_2\text{O}$, have been studied by IR spectroscopy. Using isotopic substitutions, H_2O and NH_2 vibrations have been distinguished. Stretching vibrations of isotopically isolated HDO molecules and NHD groups have been assigned.

INTRODUCTION

The crystal structure of trans-bis(DL- α -alaninato) copper(II) monohydrate is not known. The infrared spectrum has been reported earlier (refs.1-2) but no extensive discussion of the high wavenumber region has been done. The aim of this study is to find wavenumbers for the internal vibrations of the water molecule. Since those bands are partly overlapped by amino stretchings and bending, it is necessary to consider also those vibrations.

EXPERIMENTAL

The compound was prepared as reported in ref.3. Isotopic substitutions were made by recrystallization ($\text{H}\rightarrow\text{D}$) or by exchange of water molecules via the vapour phase ($^{16}\text{O}\rightarrow^{18}\text{O}$). Samples were prepared as mulls in nujol or fluorolube. Spectra were run using a Perkin-Elmer 580B spectrometer and an RIIC-VLT cryostat for the low temperature (100 K) work.

RESULTS AND DISCUSSION

Wavenumbers and assignments are given in Table 1 and the infra-

TABLE 1
Wavenumbers (cm^{-1}) for internal vibrations of the water molecule
and for stretching vibrations of the amino group.

Assignment ^a	H vibrations		D vibrations	
	100K	300K	100K	300K
$\nu_{\text{OH}}(\text{H}_2\text{O})$ or $\nu_{\text{OD}}(\text{D}_2\text{O})$	3387	3389	2528	2534
$\nu_{\text{OH}}(\text{H}_2^{18}\text{O})$	3378	3380		
$\nu_{\text{OH}}(\text{HDO})$ or $\nu_{\text{OD}}(\text{HDO})$	3369	3374	2492	2497
$\nu_{\text{OD}}(\text{HD}^{18}\text{O})$			2478	2485
$\delta(\text{H}_2\text{O})$ or $\delta(\text{D}_2\text{O})$	1674	1666	1222	1218
$\delta(\text{H}_2^{18}\text{O})$	1670	1662		
$\nu_{\text{NH}}(\text{NH}_2)$ or $\nu_{\text{ND}}(\text{ND}_2)$	3304		2471	2469
	3286	3286	2452	2469
	3260	3265	2438	2443
	3156	3156	2388	2396
		2329	2334	
$\nu_{\text{NH}}(\text{NHD})$ or $\nu_{\text{ND}}(\text{NHD})$	3236	3239	2390	2393
	3218	3224		

^aThe possibility of bending overtones has not been considered.

red spectra are shown in Figs. 1-3. The assignments are mainly based on the shifts following H-D and ^{16}O - ^{18}O substitutions. The latter makes it possible to distinguish between O-H and N-H vibrations.

The appearance of only one OH (OD) stretching band for the isotopically diluted HDO molecules, suggests that the OH vibrators present in the crystal are equivalent or that they have nearly the same environment. The isotopic ratio $\nu_{\text{OH}}(\text{HDO})/\nu_{\text{OD}}(\text{HDO})$ is 1.35 and the anharmonicity coefficient is calculated to be 237 cm^{-1} ; values which agree with earlier findings for water molecules in crystal hydrates (see correlation curves in ref. 4).

The two N-H stretching bands of the isotopically isolated NHD groups indicate at least two non-equivalent N-H bonds in the crystal.

The water bending vibration is revealed by ^{16}O - ^{18}O substitution. The wavenumber ratio $\delta(\text{H}_2\text{O})/\delta(\text{D}_2\text{O})$ is 1.37, which is normal.

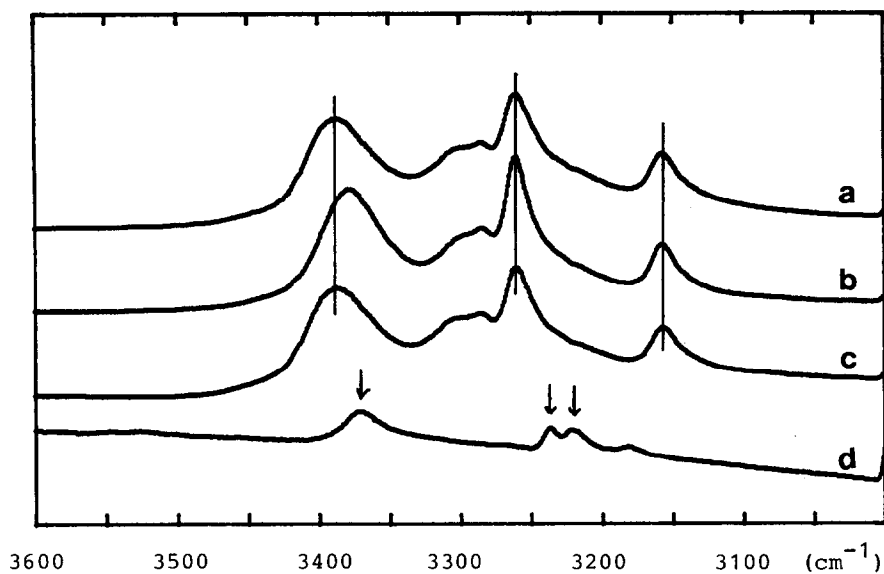


Fig. 1. IR spectra of $(\text{NH}_2\text{CH}(\text{CH}_3)\text{COO})_2 \text{Cu}(\text{II}) \cdot \text{H}_2\text{O}$ at 100 K in fluorolube mull. a) 100% H b) 98% H, 2% D, ^{18}O (water) c) 98% H, 2% D d) 2% H, 98% D. The intensity scale is in absorbance.

The intensity of spectrum d has been increased intentionally. Vertical lines are drawn to facilitate the observation of shifts. Arrows indicate bands from isotopically isolated HDO or NHD.

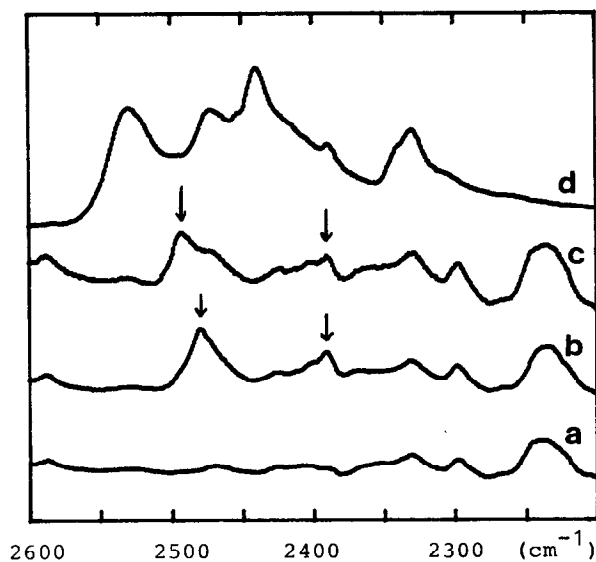


Fig. 2. See Fig.1. The intensities of a), b) and c) are increased.

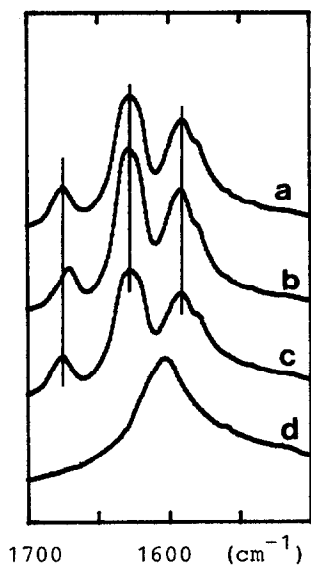


Fig. 3.

The spectra and the notation are the same as in Fig. 1.

From Fig. 3 it is evident that the NH_2 bending vibration, expected around 1600 cm^{-1} , does not appear as a single band but is considerably mixed with the COO stretching vibration.

Since the site symmetry of the species considered is not known, it is not meaningful to discuss the H_2O and NH_2 vibrations in terms of symmetric and antisymmetric vibrations. We also avoid to assign the overtones of the H_2O and NH_2 bending vibrations, which surely influence the stretching region.

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