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INFRARED SPECTRA OF DIAQUABIS(GLYCINATO-*O,N*)NICKEL(II) IN THE X-H AND X-D STRETCHING REGION

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The infrared spectra of diaquabis(glycinato-*O,N*)nickel(II) were recorded in the region 4000-250 cm^{-1}, but particular attention was paid to analysis of the X-H and X-D stretching regions (X being N or O).

1. INTRODUCTION

As a part of an extensive vibrational study of various metal complexes of amino acids [1-3], investigated were the infrared spectra of protiated and deuterated diaquabis(glycinato-*O,N*)nickel(II) (abbreviated, hereafter, $Ni(gly)_2 \cdot 2H_2O$.

The title compound crystallizes in the space group $P2_1/n$ with two molecules per unit cell [4-6]. The nickel atom is situated on a center of symmetry, so that in the unit cell there is only one type of water molecules and one type of NH_2 groups. Each water molecule forms two rather strong hydrogen bonds, the corresponding $R(O_w \cdots O)$ distances being 269.2 and 273.1 pm. According to the crystallographic data [6], only one hydrogen atom from the amino group is involved in the formation of a weak hydrogen bond (the N-H···O distance being reported as 305.3 pm), whereas the other relatively short N···O contact (313.0 pm) was not considered to represent a hydrogen bond.

Diaquabis(glycinato-*O,N*)nickel(II) and its various isotopomers have already been studied [7-9] using infrared and Raman spectroscopy and a normal coordinate analysis was performed [8,9].

To the best of our knowledge, no systematic spectroscopic study of the partially deuterated analogues has been done. It was the lack of such data that made us undertake a reinvestigation of the infrared spectra of $Ni(gly)_2 \cdot 2H_2O$, paying particular attention to the X-H and X-D stretching regions.

2. EXPERIMENTAL

$Ni(gly)_2 \cdot 2H_2O$ was prepared using a reported method [4]. The partially deuterated analogues were prepared by recrystallization of the proti-

ated compound from H_2O/D_2O mixtures of appropriate composition.

The infrared spectra were recorded at room and liquid-nitrogen temperatures on Perkin-Elmer 580 and Perkin-Elmer 580B spectrophotometers.

3. RESULTS AND DISCUSSION

The RT and LNT infrared spectra of $Ni(gly)_2 \cdot 2H_2O$ are shown in Fig. 1 and the NH/ND stretching region of samples with various deuterium content is presented in Fig. 2.

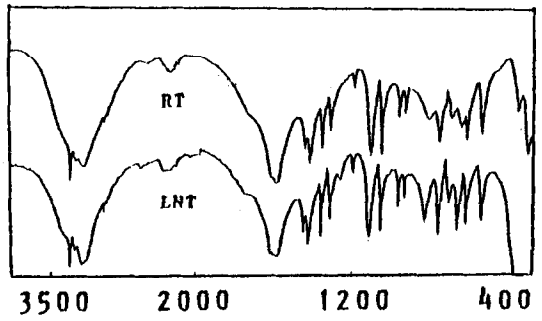

Fig. 1. RT and LNT spectra of diaquabis(glycinato-*O*,*N*)nickel(II)

As seen, in the spectrum of the protiated compound (curve 1 in Fig. 2) two sharp bands exist in the X-H stretching region, followed by a much broader feature slightly below 3300 cm^{-1}.

The high-frequency bands are shown [9] to exhibit ^{15}N-sensitivity, so that they must be attributed to the NH_2 stretching modes. Their sharpness is consistent with the weak interactions of the H-bonding type in which the amino group hydrons take part. In an analogous manner, the two sharp high-frequency bands existing in the X-D stretching region of

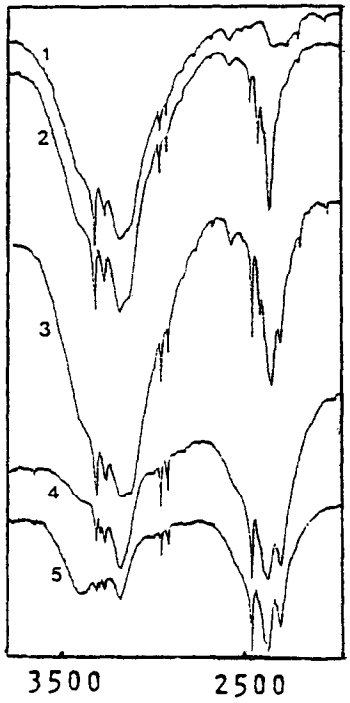

Fig. 2. The X-H and X-D stretching region in the spectra of the partially deuterated analogues of the title compound (the deuterium content increases from top to bottom)

the highly deuterated samples (curve 5 in Fig. 2) are assigned to the N-D stretchings.

Since the assignment outlined above seems unquestionable, the broad feature centered around 3300 cm^{-1} in the spectrum of the protiated compound must be assigned to the stretching vibrations of the water molecules. In a similar vein, the clearly separated bands appearing below 2400 cm^{-1} in the spectrum of the highly deuterated analogue must be related to modes in which the D_2O deuterons take part. They can be both due to the D_2O stretching fundamentals or the low-frequency component of the doublet may originate from a second-order transition interacting with one of the fundamentals.

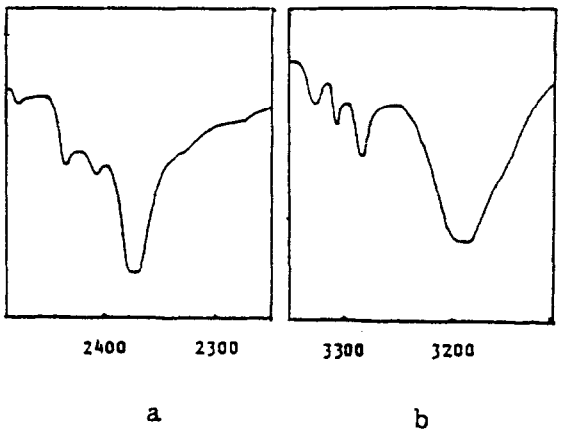

Fig. 3. The X-D and X-H stretching regions in the spectra of the slightly deuterated (a) and the highly deuterated compound (b) respectively

The fact that in the spectrum of the slightly deuterated compound (Fig. 3 a) the two O-D stretching bands are unresolved is in complete agreement with the small difference between the two O-H···O distances. In fact, the situation is similar in the X-H stretching region of the highly deuterated compound (Fig. 3 b).

The spectra of the partially deuterated samples, however, do not seem to support the hydrogen-bonding scheme proposed for the NH_2 protons in ref. [6].

If, namely, one of the NH_2 protons is "free" (i.e. not involved in hydrogen bonding) then the two bands found in the spectra of the protiated compound should be assigned to practically uncoupled N-H stretching vibrations and their frequencies would remain essentially unchanged, irrespectively of the degree of deuteration.

As seen in Fig. 3, this is *not* so. Instead of the high-frequency doublets, namely, *triplets* are observed, the central bands (that at 2442 cm^{-1} in the former and the one at 3308 cm^{-1} in the latter case) being, beyond doubt, due to the N-D and N-H vibrations of the NDH groups respectively.

The appearance of *only one* N-H and *only one* N-D stretching band attributable to the corresponding vibrations of the NDH groups is unexpected in view of the crystallographic results [6] according to which two hydrons are crystallographically non-equivalent. Under such circumstances, *two* types of semideuterated amino groups are expected to be present, depending on the site of the deuterium-for-protium substitution (we can designate these groups as DNH and HND respectively) and *pairs of bands* due to the N-H and to the N-D stretches of partially deuterated amino groups are expected to appear.

In fact, the observed spectral picture is consistent with the presence of NH_2 groups whose effective symmetry is essentially C_{2v}. In such a case, namely, the bands which are already present in the spectra of the protiated compound would be due to the antisymmetric and symmetric NH_2 stretching modes respectively, whereas the central band observed in the spectra of the partially deuterated analogues would originate from practically coincident N-H (or N-D) vibrations of the HND and DNH groups.

In other words, from a spectroscopic point of view the two hydrons of the amino groups are *effectively equivalent*.

In principle, the conclusion made above could be confirmed by the presence of a single HND bending band. The situation in the corresponding region is not sufficiently clear, but it does seem that only the band appearing around 1402 cm^{-1} in the spectra of the partially deuterated sample could be attributed to the two expected bending modes - δ(HND) and δ(DNH).

It should be noted that, as in the case of the protiated compound, in the spectra of the partially deuterated analogues (Fig. 3) the water (and HDO) bands are completely overlapped.

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