

INFRARED SPECTRA OF RUBIDIUM DIAQUATETRACHLORONICKELATE(II)

Bojan Šoptrajanov, Viktor Stefov and Marina Ivanovska

Institut za hemija, PMF, Univerzitet "Kiril i Metodij"
P.O. Box 162, 91001 Skopje, Macedonia

The infrared spectra of $\text{Rb}_2[\text{NiCl}_4(\text{H}_2\text{O})_2]$ as well as those of a series of its partially deuterated analogues were recorded at room and at liquid-nitrogen temperature (RT and LNT respectively). The combined results from the analysis of these spectra were used to assign the observed infrared bands.

1. INTRODUCTION

Continuing our work on the infrared spectra of $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ and of its cesium analogue [1,2], we decided to study the infrared spectra of the isostructural $\text{Rb}_2[\text{NiCl}_4(\text{H}_2\text{O})_2]$ and of a series of its partially deuterated analogues.

The infrared and Raman spectra of protiated $\text{Rb}_2[\text{NiCl}_4(\text{H}_2\text{O})_2]$ have already been studied (at 15 K) by Shankle and Bates [3] who listed the frequencies and assignment of the observed bands in the region from 3700 to 50 cm^{-1} . The deuterated analogues were not studied, however, and thus the opportunity to adequately assign the bands which are due to the internal and, especially, the external vibrations of the water molecules on the basis of their behaviour on partial deuteration [1,2] was missed.

It was shown ([4] as quoted in [3]) that $\text{Rb}_2[\text{NiCl}_4(\text{H}_2\text{O})_2]$ crystallizes in the triclinic system (space group $\overline{P}1$, $Z = 1$).

Only one type of water molecules, lying on general positions, are pre-

sent in the structure. The water molecules are trigonally coordinated and surrounded by a manganese(2+) ion and two chlorine atoms acting as proton-acceptors.

2. EXPERIMENTAL

The studied compound was prepared according to literature methods [3].

The deuterated analogues were prepared in a similar manner but using as solvents $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures of appropriate composition.

The infrared spectra were recorded, at room and at liquid-nitrogen temperature (RT and LNT), on a Perkin-Elmer 580 infrared spectrophotometer provided with a VLT-2 (RIIC, London) variable temperature cell.

Nujoll and fluorolube mulls and RbCl pellets were used.

3. RESULTS AND DISCUSSION

The RT and LNT infrared spectra of $\text{Rb}_2[\text{NiCl}_4(\text{H}_2\text{O})_2]$ recorded between 4000 and 350 cm^{-1} are presented in

Fig. 1. In line with the expectations based on the existing structural similarities [4,5], the spectra are very similar with those of rubidium diaquatetrachloromanganate and especially those of its cesium analogue [1,2].

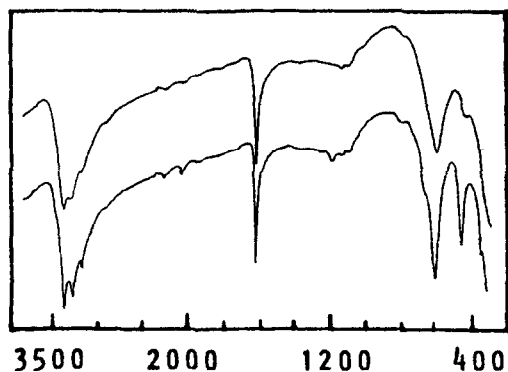


Fig. 1. RT and LNT spectra of rubidium diaquatetrachloronickelate(II)

As can be seen, *three* (two stronger and one weak) bands exist in the O-H stretching region of the spectra of the protiated compound, as well as in the O-D stretching region of the spectra of the almost completely deuterated analogue (Fig. 2) and in those of rubidium and cesium diaquatetrachloromanganates [1].

On the other hand, the appearance of single $\delta(\text{H-O-H})$ and $\delta(\text{D-O-D})$ bands (at ≈ 1625 and 1195 cm^{-1} respectively; cf. Fig. 3) is indicative of the existence of a single type of water molecules in the studied compound. So, the third band observed in the corresponding stretching regions must be due to a second-order transition (by all means, one involving the bending mode of the water molecules and probably intensified by vibrational interactions with the fundamental $\text{H}_2\text{O}/\text{D}_2\text{O}$ stretching modes). Such a conclusion is suppor-

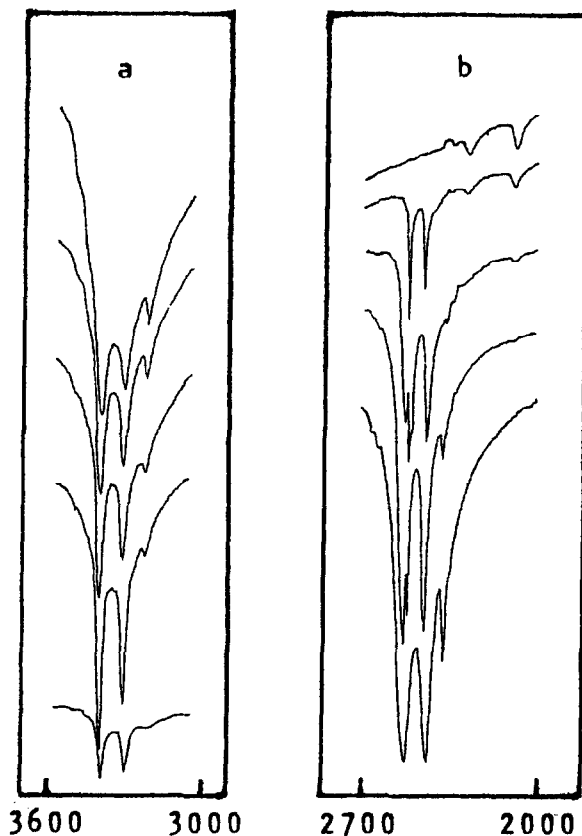


Fig. 2. The O-D (a) and O-H (b) stretching regions in the spectra of the partially deuterated analogues of rubidium diaquatetrachloronickelate(II) (the deuterium content in this and the following figures increases on going from top to bottom)

ted by the absence of such bands in the O-H region of the spectra of highly deuterated samples or the O-D stretching region in the spectra of samples with very low deuterium content, i.e. in cases when isotopically isolated HDO molecules exist in the structure.

The presence of *two* OH or OD stretching bands (at ≈ 3393 and 3300 cm^{-1} and at 2519 and 2457 cm^{-1} respectively; see Fig. 1) is in agreement

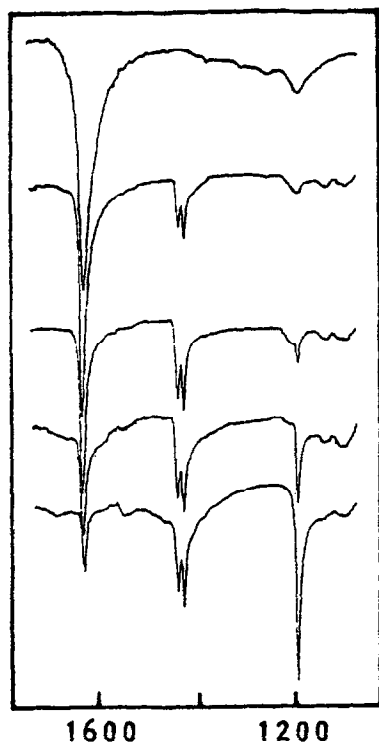


Fig. 3. The $\delta(\text{HOH})$, $\delta(\text{HOD})$ and $\delta(\text{DOD})$ bending regions in the spectra of the partially deuterated analogues of rubidium diaquatetrachloronickelate(II)

with the non-equivalence of the two hydrogen bonds formed by the water molecules.

The appearance of two $\delta(\text{H-O-D})$ bands (at ≈ 1435 and 1428 cm^{-1} ; compare Fig. 3) also shows that the protons are not equivalent. The situation is, as mentioned above, similar in the case of rubidium and cesium diaquatetrachloromanganates [1].

It should be noted that Shnakle and Bates [3] explained the presence of the 3223 cm^{-1} band (i.e. the band at lowest frequency among those appearing in the O-H stretching region) in

their spectra of $\text{Rb}_2[\text{NiCl}_4(\text{H}_2\text{O})_2]$ by assuming the existence of extra degrees of vibrational freedom.

Three bands of librational origin are found in the infrared spectra of $\text{Rb}_2[\text{NiCl}_4(\text{H}_2\text{O})_2]$ and those of its almost completely deuterated analogue (see Figs. 4 and 5) whereas Shnakle and Bates [3] found only two such bands.

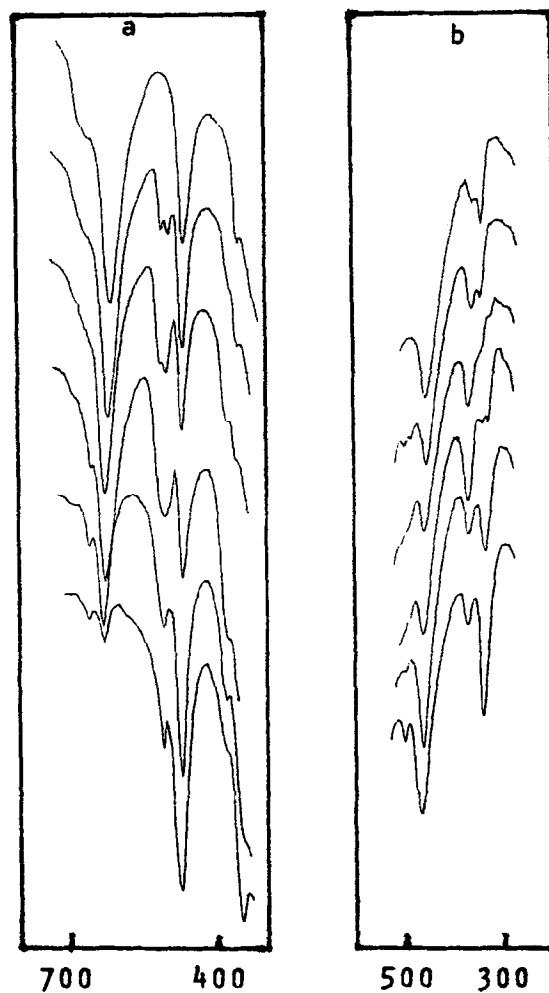


Fig. 4. The low-frequency region in the LNT spectra of the partially deuterated analogues of rubidium diaquatetrachloronickelate recorded with KBr windows (a) and polyethylene windows (b) in the VLT-2 cell

As in the case of rubidium and cesium diaquatetrachloromanganates [2], on the basis of its behaviour on partial deuteration, the band having the lowest frequency can be attributed to a mode which is essentially rocking in character.

The remaining two librational modes are then the result of the partial mixing of the twisting and wagging modes. For the HDO molecules, the two out-of-plane (oop) librations are mixed to a much higher degree, giving rise to modes which are best described as oop motions of the proton and the deuteron respectively (the so-called "H-motion" and "D-motion").

The order of the librational frequencies would then be twisting > wagging > rocking. It should be pointed out that this order does not agree with that predicted on the basis of the model calculations of Eriksson and Lindgren [6] for trigonally coordinated water molecules.

The results of the assignment of the librational bands in the isotopomers of rubidium diaquatetrachloronickelate(II) are summarized in Fig. 5.

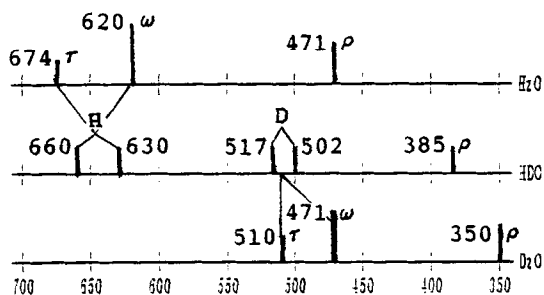


Fig. 5. Position and intensity of the water librational bands in the spectra of the title compound isotopomers

The band appearing at 364 cm^{-1} in the spectrum of $\text{Rb}_2[\text{NiCl}_4(\text{H}_2\text{O})_2]$ and at $\approx 350 \text{ cm}^{-1}$ in the spectrum of its almost completely deuterated analogue (Fig. 5) could be assigned to the nickel-water stretching. The small value for the ratio of the D_2O and H_2O frequencies may be taken as an evidence that this assignment is correct. It is fair to add that in the spectra of the samples deuterated to a high degree the metal-to-water stretching band is overlapped with the intense band due to the D_2O rocking mode.

ACKNOWLEDGEMENT

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