FOURIER-TRANSFORM INFRARED SPECTRA OF *cis*-DI(THIOCYANATO)BIS(2,2'-BIPYRIDYL-4,4'-DICARBOXYLATE)RUTHENIUM(II) DIHYDRATE - A CHARGE-TRANSFER SENSITIZER ON NANOCRYSTALLINE TiO_2 ELECTRODES

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INTRODUCTION

Monolayers of certain dyes can be used to cover the surface of wide band-gap semiconductors such as colloidal (nanocrystalline) TiO_2 films employed as electrodes, increasing, in some cases dramatically, the degree of conversion of photons into electrical current. It was shown [1] that when certain colored *complexes* (particularly those of ruthenium and osmium) are used, the sensitizing effect is more pronounced. In order to be an efficient sensitizer, the complex should be able to undergo light-induced electron injection from its excited state into the conduction band of the semiconductor (the absorption of visible light is related to a metal-to-ligand charge-transfer transition). In this way it is possible to produce relatively inexpensive, long-lasting and efficient TiO_2 solar cells (Grätzel-type cells). Among the ruthenium complexes which have been tested so far, the title compound – *cis*-di(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) dihydrate – has been shown [2] to exhibit the most remarkable efficiency as a sensitizer. Some fragmentary data on the Fourier-transform infrared (FTIR) spectra of this compound are given in Ref. 2.

Since two of us (B.Š. and M.T.) have been, for quite some time, involved in the study of the infrared spectra of bipyridine complexes, on the one hand, and of crystallohydrates, on the other [3-7], it seemed natural to attempt to study, in somewhat more detail than previously done [2], the FTIR spectra of the title compound. It was decided to pay particular attention to the regions where the thiocyanato and the water bands are expected to appear.

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EXPERIMENTAL

The studied compound was prepared as previously [2] described.

The Fourier-transform infrared spectra were recorded, from KBr pellets, on a Perkin-Elmer 2000 FTIR system both at room temperature (RT) and at temperatures down to the boiling temperature of liquid nitrogen (LNT), the latter measurements being particularly important in the course of the study of bands arising from external vibrations of the water molecules.

RESULTS AND DISCUSSION

The RT and LNT spectra of *cis*-di(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) dihydrate are shown in Fig. 1.

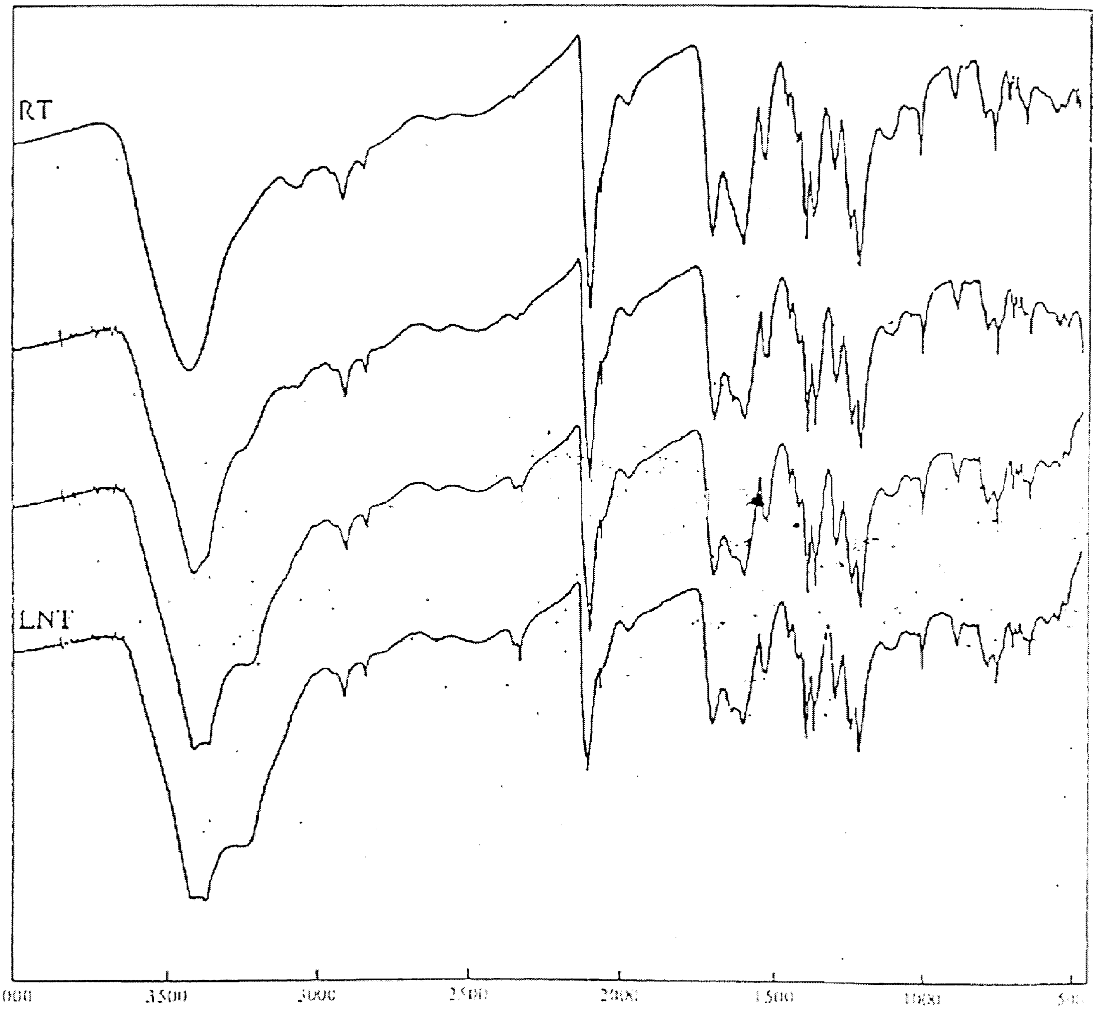

Fig. 1. FTIR spectra of *cis*-di(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) dihydrate recorded from RT down to LNT

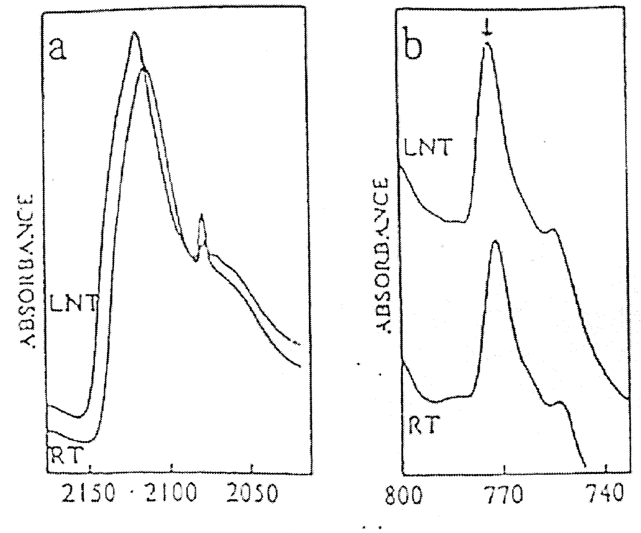

Fig. 2. Infrared spectra in the regions of the two stretching vibrations of the N=C=S⁻ group

Taking into account the complexity of the building units (bipyridine moieties, carboxylate and thiocyanate groups, water molecules) as well as the expected low overall symmetry for the complex as a whole, the spectra are surprisingly simple. However, all the characteristic spectral features of the structural units *are* present as will be shown for the case of the bands to be discussed in more detail below. As Figs. 1 and 2 show, a strong band (or, rather, a practically unresolved doublet) followed by a much weaker satellite is found in the 2150-2100 cm^{-1} region of the spectra. It should, perhaps, be pointed out that we were unable to find *two* separate bands (at 2126 and 2093 cm^{-1}) in this region as previously [2] reported. It is easily seen that the strong band is temperature-sensitive and shifts towards higher frequencies when the temperature is lowered. Whereas the strong band undoubtedly arises from one of the thiocyanate stretching vibrations, it is practically certain that the weak band is due to a second-order transition of some sort. Such a conclusion is based not only on the intensity of the satellite, but also on its independence on the temperature.

The frequency of the strong band (2117 cm^{-1} is the value for the main peak at LNT) is consistent with the assumption of *N*-bonded thiocyanato groups in the structure. In line with such a conclusion are the frequency and the intensity of the band appearing around 772 cm^{-1} already observed and assigned to a mode which is predominantly C=S stretching in character [2]. It is, thus, almost certain that the thiocyanato groups are indeed bonded to the ruthenium atom via their nitrogen end.

The results of the elemental analysis of the title complex [2] indicated that the compound is a dihydrate. This is somewhat surprising since one expects that with four nitrogen atoms from the two bipyridine rings and two nitrogen atoms from the two thiocyanato groups, the co-ordination sphere around the ruthenium atom would be complete and that water molecules would not be able to enter it. However, the spectra unequivocally show that water molecules are indeed present and that they form an integral part of the structure of the studied compound. Namely, in both the RT and LNT spectra, strong bands are seen in the region where the stretching vibrations of the water molecules are expected to appear (Fig. 3a). The main maximum in the RT spectra is found around 3400 cm^{-1}, accompanied by an almost invisible shoulder at lower frequencies. On the other hand, at LNT the high-frequency band is clearly split into at least two components and the lower-frequency shoulder becomes clearly visible (and, apparently, also split). Such a behaviour is strongly indicative of presence of water individual complex molecules. The hydrogen bonds are, obviously, of different strength. The high-frequency LNT doublet must be due to the OH stretching vibrations of groups whose protons form relatively weak bond, whereas considerably stronger hydrogen bonds are responsible for the appearance of the lower-frequency components of the complex feature found in the ν(OH) region..

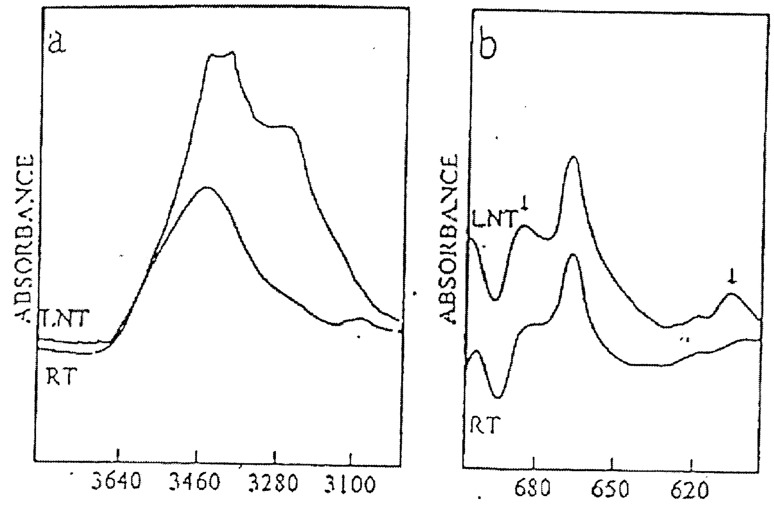

Fig. 3. The infrared spectra in the regions of water stretchings (a) and water librations (b)

That the water molecules form an integral part of the structure is even more clearly demonstrated by the appearance of at least two bands which are practically invisible at RT but gain considerably in intensity and shift towards higher frequencies when the temperature is lowered down to LNT (Fig. 3b). The described temperature behaviour is, namely, characteristic of bands which are due to librations (hindered rotations) of structural water molecules be they co-ordinated *and* hydrogen-bonded or only hydrogen-bonded.

REFERENCES

1. B. O'Regan, M. Grätzel, *Nature*, 353, 737 (1991).
2. M.K. Nayeeruddin, A. Kay, I. Rodicio, R. Humphry-Bakker, E. Müller, P. Liska, N. Vlachopulos, M. Grätzel, *J. Amer. Chem. Soc.*, 115, 6382 (1993).
3. I. Petrov, B. Šoptrajanov, *Spectrochim. Acta*, 31A, 309 (1975).
4. M. Trpkovska, B. Šoptrajanov, *Vestn. Sloven. Kem. Društva*, 33 Suppl., 41 (1986).
5. B. Šoptrajanov, M. Trpkovska, *J. Mol. Struct.*, 267, 185 (1992).
6. M. Trpkovska, B. Šoptrajanov, *Croat. Chem. Acta*, 65, 179 (1992).
7. B. Šoptrajanov, M. Trpkovska, *J. Mol. Struct.*, 293, 109 (1993).