

DERIVATIVE INFRARED SPECTRA OF REINECKATES OF N-ORGANIC BASES

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Derivative infrared spectra in CN stretching range ($1800-2200\text{ cm}^{-1}$) for twenty two reineckates of N-organic bases ($\text{HL}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$), where HL are protonated N-organic bases are studied and interpretation is made on the basis of crystal structure of ammonium and pyridinium reineckates. It is concluded from this work that the number of CN stretching bands correspond to the number of thiocyanate groups with different mode of behaviour in the crystal lattice.

Key words: Infrared spectra, Reineckates.

INTRODUCTION

In previous investigations [1-6] the reineckates of aliphatic and aromatic mono- and diamines as well as the reineckates of phenothiazine and phenoazepine derivatives were studied and their electronic and infrared spectra were discussed. Interpretations of these salts were mostly made on the basis of pseudosymmetric stretching vibration $\nu_{\text{C-N}}$, because this vibration is more sensitive to counter ions [7].

In this paper derived infrared spectra in $1800-2200\text{ cm}^{-1}$ range are discussed. The choice of this range is made because there is no vibration from N-organic bases which can interfere with CN stretching vibration. The interpretation of the derived CN stretching vibrations are made as:

Reineckates of aliphatic N-organic bases

Reineckates of aromatic N-organic bases

Reineckates of phenothiazine and phenoazepine derivatives

MATERIALS AND METHODS

Reagents were used as reported previously [1-4]. The derivative infrared spectra in $1800-2200\text{ cm}^{-1}$ range were recorded on specord 75-IR "on line" KSR - 4100, Carl Zeiss Jenna (G.D.R.).

The salts were prepared by the method described previously [1-4].

RESULTS AND DISCUSSION

The $\nu_{\text{C-N}}$ bands obtained by second differential method are given in Table 1.

For the interpretation of $\nu_{\text{C-N}}$ bands of all reineckates, the bands of the reineckates with known crystal structures, $[\text{NH}_4][\text{RS}]$ and $[\text{pyH}][\text{RS}]$, are considered first. In the case of $[\text{NH}_4][\text{RS}]$, five bands are observed for CN

stretching vibration by second differential method. It is known [8] from the crystal structure of the salt that NH_4^+ ion at the body centred position is surrounded by six sulphur atoms octahedrally with distance of 3.35 \AA . The water molecules at the corners of the cube are surrounded by twelve sulphur atoms with a distance of 4.44 \AA . From the analysis of the projected unit cell, it is observed that some sulphur atoms of NCS groups are directed to NH_3 groups or to the atoms of N or S of the other NCS groups. It is presumed that in crystal lattice there are five groups of non-equivalent thiocyanates and the five bands of $\nu_{\text{C-N}}$ correspond to these groups. This proposition is further supported by the crystal structure of pyridinium reineckates [9]. For this salt also $\nu_{\text{C-N}}$ has five bands which are interpreted as follows: The reineckate groups are linked together around the two-fold screw axis, resulting in a frame-like structure with large holes around the two-fold axis, and pyridinium ions are situated in these holes. The atomic distances between the sulphur of NCS groups and different atoms or radicals are: $\text{N}_3\text{-S}_1 = 3.36$, $\text{C}'_3\text{-S}_1 = 3.38$, $\text{C}'_3\text{-S}'_2 = 3.47$, $\text{N}_3\text{-S}'_2 = 3.60$, $\text{NH}_3\text{-S}'_2 = 3.60$, $\text{NH}_3\text{-S}'_1 = 3.61$, $\text{C}_4\text{-S}_2 = 3.82$, $\text{C-S}_1 = 4.33$ and $\text{C}_4\text{-S}'_1 = 4.34\text{ \AA}$. According to Takeuchi and Pepinsky [9] four sulphur atoms are coordinated to the pyridinium nitrogen (N_3) with distances of 3.36 and 3.60 \AA . Other sulphur atoms are directed to carbon atoms or NH_3 groups. From the atomic distances it is concluded that in the crystal lattice of pyridinium reineckate there are nine groups of NCS with the sulphur end directed to different atoms. But in some cases the atomic distances are the same or nearly the same, e.g., $\text{N}_3\text{-S}'_2$ and $\text{NH}_3\text{-S}'_2 = 3.60\text{ \AA}$, whereas $\text{NH}_3\text{-S}'_1 = 3.61$ and $\text{C-S}_1 = 4.33$, whilst $\text{C}_4\text{-S}'_1 = 4.34\text{ \AA}$. It is proposed that the five bands of $\nu_{\text{C-N}}$ are due to the interaction of sulphur from NCS and atoms of pyridine or NH_3 groups. When atomic distances are the same or nearly the same, then probably clear separated bands are not observed. The

five bands observed for CN stretching are assigned to the following interacting groups of NCS: (1) $N_3-S_1=3.36$ and $C'_3-S'_1=3.38$, (2) $C'_3-S'_2=3.47$, (3) $3-S'_2=3.60$, $NH_3-S'_2=3.60$ and $NH_3-S'_1=3.61$, (4) $C_4-S_2=3.82$ and (5) $C-S_1=4.33$ and $C_4-S'_1=4.34$ Å. It is assumed that bands with higher frequencies belong to NCS groups having shorter distances with the interacting atoms and vice versa.

Considering the above facts explained on the basis of crystal structures the CN stretching bands for other reineckates are interpreted as follows.

Reineckates of aliphatic N-organic bases. The ν_{C-N} bands for reineckates of aliphatic N-organic bases are given in Table 1a. Four bands with different positions are observed

Table 1. Band position of CN stretching vibration* (cm^{-1}).

(a) Reineckates of aliphatic N-organic bases	
Compound	ν_{C-N}
[NH ₄][RS] 2/3 H ₂ O	2131, 2121, 2102, 2085, 2048
[enH][RS]	2126, 2112, 2098, 2077
[tnH][RS]	2127, 2102, 2079, 2062
[pdnH][RS]	2127, 2109, 2095, 2088 sh, 2066
[pnH][RS]	2126, 2110, 2073, 2069
[n-banH][RS]	2123, 2116, 2102, 2073
[sec-banH][RS]	2114, 2102, 2086, 2074
[teanH][RS]	2122, 2102, 2085, 2054
(b) Reineckates of aromatic N-organic bases	
[pyH][RS]	2127, 2103, 2087, 2076, 2040
[dipyH][RS]	2128, 2106, 2092, 2082, 2057
[O-phenH][RS]	2112, 2100, 2084 b
[anH][RS]	2124, 2107, 2092, 2069, 2047
[benznH][RS]	2124, 2104, 2096, 2079, 2068
[O-tldH][RS]	2110, 2097, 2084, 2066
(c) Reineckates of phenothiazine and phenazepine derivatives	
[prznH][RS]	2124, 2099, 2060, 2051
[prtznH][RS]	2116, 2094, 2056 b
[cprznH][RS]	2106, 2090, 2062
[trdznH][RS]	2106, 2088, 2065
[pznH ₂][RS] ₂	2121, 2101, 2067, 2061
[cpznH ₂][RS] ₂	2122, 2112, 2086, 2062
[ipnH][RS]	2094, 2076, 2049
[oplH ₂][RS] ₂	2126, 2108, 2086, 2076

*Abbreviations used: RS = Reinecke's salt anion, en=ethylene diamine, tn=trimethylenediamine, pdn=pentamethylenediamine, pn=1, 2-propanediamine, ban=butylamine, tean=triethylamine, py=pyridine, dipy-2, 2-dipyridyl, o-phen=1, 10-phenanthroline, an=aniline, benzn=benzylamine, o-tld=o-toluidine, przn=diphenylthiazine-promazine, prtzn=diphenylthiazine-promethazine, cprzn=diphenylthiazine-chloropromazine, trdzn=diphenylthiazine-thioridazine, pzn=diphenylthiazine-pyrazine, cpzn=diphenylthiazine-chloropyrazine, ipn=diphenylazepine-imipramine, opl=diphenylazepine-opipramol.

for all these reineckates. The highest frequency band for diamine reineckates, [enH][RS], [tnH][RS], [pdnH][RS] and [pnH][RS] is at 2126, 2127, 2127 and 2126 cm^{-1} respectively which are rather at the same position and the same band for monoamine reineckates, [n-banH][RS], [sec-banH][RS] and [teanH][RS] is at 2123, 2114, and 2122 cm^{-1} respectively. It is concluded that hydrogen bonding with the amino group in the diamine reineckates is stronger than the hydrogen bonding in monoamine.

The comparison of [n-banH][RS] and [sec-banH][RS] shows that the branching of the chain also influences the nature of interaction and, therefore, the highest frequency band is obtained at 2123 and 2114 cm^{-1} respectively.

The lower frequency bands in the above reineckates are assigned to the hydrogen bonding of the type Cr-NCS---H-C-. It is found [10] that the aliphatic diamines in the crystal lattice are not in a straight chains form but curves. Therefore, it is easier for the hydrogens, bonded to carbon atoms, to interact with the free sulphur end of NCS, where the orientation of cations in the crystal lattice also influences the nature of interaction as reported for the choline reineckate in which protonated choline has four possible orientations in the crystal lattice [8].

Reineckates of aromatic N-organic bases. The band positions for CN stretching vibrations are given in Table 1b where the spectra in ν_{C-N} range for three reineckates, [dipyH][RS], [phenH][RS] and [o-tldH][RS] are shown in Fig. 1.

Mostly the reineckates of aromatic N-organic bases have five bands for ν_{C-N} with the exception of [phenH]-

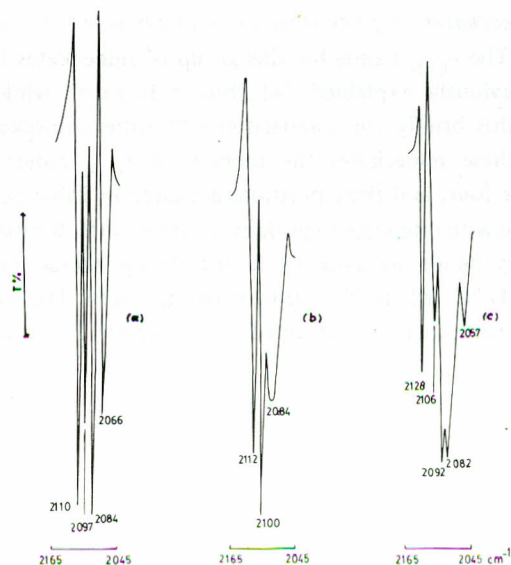


Fig. 1. Characteristic ν_{C-N} bands for (a) [o-tldH][RS], (b) [phenH][RS] and (c) [dipyH][RS].

[RS] and [o-tldH] [RS] which have three and four bands respectively. But the band at 2084 cm^{-1} for [phenH] [RS] is very broad (Fig. 1) and presumably it has more components which could not be separated at this stage.

It has been already explained on the basis of crystal structure that there are hydrogen bondings in all reineckates due to which the $\nu_{\text{C-N}}$ band is split and the position of the bands corresponds to the strength of these hydrogen bondings.

The number of $\nu_{\text{C-N}}$ bands in [dipyH] [RS], [anH] [RS] and [benznH] [RS] are the same as in pyridinium reineckate where small differences in their positions are observed and are presumably due to different strengths of hydrogen bonding with NCS groups. Therefore, it is concluded that their structures are rather similar to pyridinium reineckate. The nature of bands in [o-tldH] [RS] are interesting. The highest frequency band at 2110 cm^{-1} is lower than other reineckates in this series (reineckates of aromatic N-organic bases). It is noted that [o-tld H]⁺ is the only cation in this series which has substitution at the ring along with the amino group, and influences the strength of hydrogen bonding due to which the highest frequency band is at 2110 cm^{-1} . It is also obvious, that if the nature of bands are compared for [anH] [RS], [benznH] [RS] and [o-tldH] [RS], the cations in the former two reineckates have nearly same influence while in the latter, substitution at the cation alters the nature of interaction and so the position of bands are changed.

It is concluded that the size of the cations has less influence on CN stretching vibration but substitution at the cation alters the nature of interaction due to inductive effect.

Reineckates of phenothiazine and phenoazepine derivatives. The $\nu_{\text{C-N}}$ bands for this group of reineckates have been previously explained [4], but it is worth while to discuss this briefly for comparison with other reineckates.

In these reineckates the number of $\nu_{\text{C-N}}$ bands are three or four, and their positions are given in Table 1c. As explained with reference to pyridinium reineckate, the higher frequency bands are assigned to the strong interaction of $\text{CrNCS}---\text{H-N}^+$, where N^+ is protonated nitrogen. The bands of lower frequencies are assumed to correspond to the weak

hydrogen bonding of the type $\text{Cr-NCS}---\text{H-C}\leq$ and the differences in their positions are due to differences in the strength of bondings.

CONCLUSIONS

It is concluded from the above that:

(i) The number of $\nu_{\text{C-N}}$ bands correspond to the number of NCS group with different behaviour in crystal lattice.

(ii) The highest frequency band in all reineckates is assigned to the interaction of $\text{CrNCS}---\text{H-N}^+$, where N^+ is protonated nitrogen in the cations. The lower frequency bands are assigned to the hydrogen bonding of the type $\text{CrNCS}---\text{H-C}\leq$.

(iii) Substitution at the cations alters the nature of interaction as also the positions of $\nu_{\text{C-N}}$ bands due to inductive effect.

(iv) Hydrogen bonding with protonated nitrogen in the diamine reineckates is stronger than in the monoamine reineckates.

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