PIPERIDINIUM NITRATE – STUDY OF THERMAL BEHAVIOUR AND VIBRATIONAL SPECTRA

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Received August 31, 2005
Accepted December 13, 2005

Dedicated to Professor Jaroslav Podlaha on the occasion of his 70th birthday.

Piperidinium nitrate was studied by FTIR and FT Raman spectroscopy in the range 100–4000 cm^{-1} at 300 K. On the basis of DSC measurements which exhibit two effects indicating phase transition at 256 and 295 K, FTIR spectra were recorded down to a temperature of 90 K. Discussion of the phase transition mechanism is based on the observed changes in the FTIR spectra during cooling of the compound.

Keywords: Nitrates; Piperidinium salts; Vibrational spectroscopy; Thermal behaviour; Phase transition; DSC; IR spectroscopy; Raman spectroscopy.

The attention focused on piperidinium salts, within the research field of compounds with significant physical properties, increased after the discovery of a novel class of non-linear optical materials combining a cation derived from polarisable organic molecule with an inorganic anion capable of forming strong hydrogen-bonded crystal structures[1]. Piperidinium dihydrogen phosphate[1] was one of the first materials in this class where the efficiency of the second harmonic generation (SHG) was studied.

Another area of study of piperidinium salts is the research focused on the materials with interesting dielectric properties. Motivation of the study[2] of piperidinium haloantimonates(III) and -bismuthates(III) is the close relationship with simple halo-salts of pyridinium[3–5] where ferroelectric properties were revealed in low-temperature phases.

Piperidinium nitrate (PDN) was studied[6] for the first time from the viewpoint of the existence of the crystal stucture mesophase. In this phase (phase **I**, $T > 298$ K) both cations and anions exhibit isotropic rotations re-

Collect. Czech. Chem. Commun. 2006, Vol. 71, No. 2, pp. 207–214

doi:10.1135/cccc20060207

sulting in orientational disorder. The crystal structure of the mesophase was determined from powder X-ray diffractions as an NaCl-type cubic lattice (a = 9.39(5) Å, Z = 4, V = 827(14) Å^3, D = 1.19(2) Mg m^{-3}). However, to our knowledge, there are no crystallographic data concerning low-temperature phase(s) of PDN.

This work, which is a part of our project dealing with the preparation and study of new non-linear optical materials based on salts of organic nitrogen bases with inorganic oxoacids, is focused on vibrational spectroscopic and DSC study of PDN in wide temperature range. Discussion of the phase transition mechanism is based on FTIR data as we were unsuccessful in preparation of a single crystal suitable for X-ray structure analysis.

EXPERIMENTAL

Synthesis

Crystals of PDN were prepared by slow spontaneous evaporation of a solution obtained by mixing of piperidine (99%, Aldrich) and nitric acid (p.a., Lachema, 2 mol dm^{-3}) in equimolar ratio at room temperature. The colourless crystals obtained were collected under vacuum on an S3 frit, washed with a small amount of ethanol and dried in a desiccator over solid KOH. Elemental analysis results for C, H and N (40.5% C, 7.9% H, 19.1% N) agree with the theoretical content (40.5% C, 8.2% H, 18.9% N).

Characterisation

The infrared spectra in nujol and fluorolube mulls were recorded on a Nicolet Magna 760 FTIR spectrometer with 2 cm^{-1} resolution (4 cm^{-1} resolution in far-IR region) and Happ–Genzel apodization in the 100–4000 cm^{-1} range. Low-temperature measurements were carried out by the nujol mull method in low-temperature cell with KBr or PE windows in the 300–90 K interval. The temperature was measured with a Fe–Constantan thermocouple. The analog signal was processed on a PC using the AX5232 temperature measurement board.

The Raman spectrum of polycrystalline sample was recorded on a Bruker Equinox 55/S FTIR spectrometer with a FRA 106/S Raman module (2 cm^{-1} resolution, Blackman–Harris 4-Term apodization, 1064 nm NdYAG laser excitation, 250 mW power at the sample) in the 100–4000 cm^{-1} region at 300 K.

The DSC measurements were carried out on a Perkin–Elmer Pyris Diamond DSC instrument at 95–323 K in dinitrogen atmosphere (20 ml min^{-1}). A heating rate of 10 K min^{-1} was selected to measure ca. 15 mg of finely ground sample placed in hermetically sealed aluminium pans.

RESULTS AND DISCUSSION

Vibrational Spectra

The vibrational spectra of PDN are depicted in Figs 1–3 and the wavenumbers of the maxima are given in Table I (abbreviations: s, strong; m, medium; w, weak; b, broad; sh, shoulder; ν, stretching; δ, deformation or

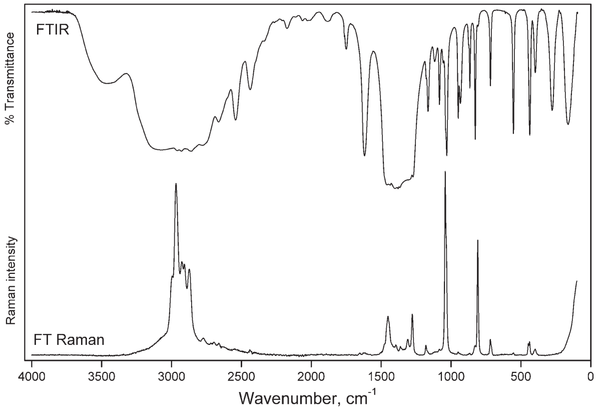

FIG. 1
FTIR (compiled from nujol and fluorolube mulls) and FT Raman spectra of piperidinium nitrate at 300 K

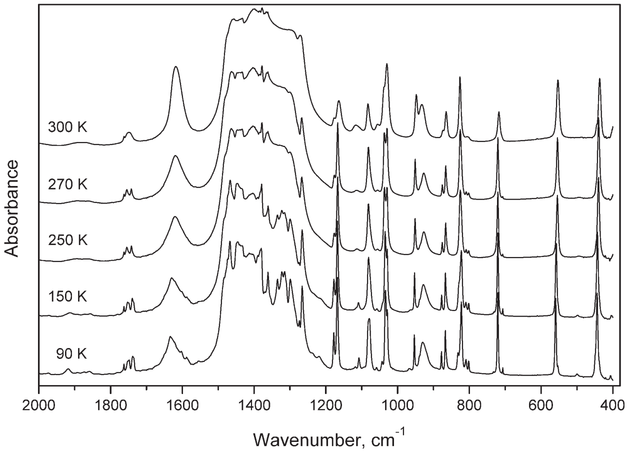

FIG. 2
FTIR spectra (nujol mull) of piperidinium nitrate at different temperatures

in-plane bending; γ, out-of-plane bending; ρ, rocking; ω, wagging; twi, twisting; as, antisymmetric; s, symmetric). The assignment of vibrational bands of the compound is mainly based on previous spectroscopic study of piperidinium halobismuthates(III) and -antimonates(III)[2].

The broad structured band in the 3700–2200 cm^{-1} region, which is more intense in the IR spectrum, corresponds to the stretching vibration of NH_2^+ group probably participating in hydrogen bonds of the N–H···O and N–H···N types. According to the position of this band (see Novak[7] and Lautie et al.[8]), the length of these H-bonds can be estimated to be 3.20–2.75 and 3.20–2.95 Å, respectively. The existence of such hydrogen bonds is also indicated by the position of $\delta(NH_2^+)$ band (1619 cm^{-1}) which is shifted in the IR spectrum by +46 cm^{-1} compared with piperidinium pentachlorobismuthate(III)[2]. Another vibrational manifestation of the NH_2^+ group is the medium to weak intense band at 933 cm^{-1} in the IR spectrum, which can be assigned[7] to out-of-plane bending vibrations γ(NH).

The sharp bands in the 3000–2800 cm^{-1} region are characteristic of stretching vibrations of CH_2 groups. Manifestations of deformation, wagging, twisting and rocking vibrations of these groups are localised in the 1460–1435, 1385–1270, 1180–1110 and 880–865 cm^{-1} regions, respectively. The bands recorded in the range of 1080–1030 and 810–440 cm^{-1} are most probably of skeletal vibration origin. The wide asymmetric band in the IR spectrum located in the 1500–1250 cm^{-1} region is the product of overlapping of the most intense nitrate band (ν_3) and bands of $\omega(CH_2)$ vibrations.

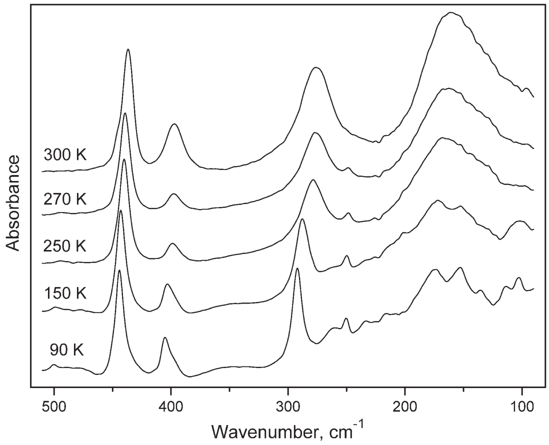

FIG. 3
FTIR (far-IR) spectra (nujol mull) of piperidinium nitrate at different temperatures

TABLE I
FTIR and FT Raman spectra of piperidinium nitrate (in cm^{-1})

IR		Raman (intensity)	Assignment
300 K	90 K	300 K	
3460 wb	3360 sh		$\nu(NH_2^+)$
	3254 w		
	3105 m		
3080 sb	3040 sb		
		2995(44)	$\nu_{as}(CH_2)$
2960 s	n.o.[a]	2968(94)	
2930 s	n.o.[a]	2926(51)	$\nu_s(CH_2)$
		2908(50)	
2857 s	n.o.[a]	2873(47)	
2775 s, 2760 s, 2740 s, 2662 m, 2542 m, 2436 w, 2174 w, 2062 w, 2020 w, 1882 w	2780 s, 2760 s, 2670 m, 2637 m, 2549 m, 2449 w, 2350 w, 2324 w, 2187 w, 2073 w, 2059 w, 2040 w, 1919 w	2772(10), 2697(8), 2662(7), 2440(4)	combination bands, overtones
1763 w	1763 w		$\nu_1+\nu_4(NO_3^-)$
1750 w	1749 w		
	1738 w		
		1653(2)	$\delta(NH_2^+)$
1619 m	1633 w	1620(2)	
1457 s	1467 s	1451(22)	$\delta(CH_2)$
	1445 s		
1435 s	1435 s		
1400 s	1410 s	1395(7)	$\nu_3(NO_3^-)$
1385 s	1389 s		$\omega(CH_2)$
1367 s			
1362 s	1361 s	1362(6)	
	1335 s		$\nu_3(NO_3^-)$, $\omega(CH_2)$
	1322 s		
1310 sh	1315 s	1309(9)	
	1299 s		
1272 s	1274 m	1277(23)	$\omega(CH_2)$
	1265 s		
1177 w	1177 m	1179(6)	twi(CH_2)
1164 m	1168 s		
1117 w	1108 w		
1083 m	1079 m	1083(4)	skeletal
	1043 w	1042(100)	$\nu_1(NO_3^-)$
1038 sh	1034 m	1035 sh	skeletal
1030 m	1029 m		

TABLE I
(*Continued*)

IR		Raman (intensity)	Assignment
300 K	90 K	300 K	
948 m	953 w	949(3)	?
933 m	930 w		γ(NH)
	878 w		$\rho(CH_2)$
865 w	867 m	867(2)	
827 m	831 w	827(6)	$\nu_2(NO_3^-)$
	822 m		
	809 w	809(63)	skeletal
804 w	802 w		
718 w	720 m	719(9)	$\nu_4(NO_3^-)$
	707 w		?
554 m	559 m	553(2)	skeletal
	444 m	447(7)	
436 m		438(8)	
397 w	405 w	398(4)	?
277 m, 162 m	355 w, 292 m, 262 w, 250 w, 175 w, 153 w, 114 w, 103 w		external modes

[a] Not observed due to nujol bands.

Very characteristic for the nitrates is the presence of weak IR active combination band of $\nu_1 + \nu_4$ (NO_3^-) vibration at about 1750 cm^{-1}. The most intense band in the Raman spectrum at 1042 cm^{-1} corresponds to $\nu_1(NO_3^-)$ vibration. The bands of ν_2 and ν_4 vibrations are located at 827 and ~720 cm^{-1} in both types of spectra, respectively.

Thermal Behaviour

Crystals of PDN are stable in air up to 423 K when melting accompanied by decomposition starts[6]. Two anomalies – weak (onset 256 K, ΔH = 0.28 kJ mol^{-1}) and strong (onset 295 K, ΔH = 5.74 kJ mol^{-1}) – were recorded on DSC curve during the first heating run of PDN starting at 90 K. Subsequent cooling run exhibits practically only the strong anomaly (onset 293 K, ΔH = –5.73 kJ mol^{-1}); the weak one at 259 K almost disappeared (see Fig. 4). Multiple repetition of the heating-cooling cycle leads to a decrease in weak anomaly intensity; a shift to higher temperatures of strong anomaly was also observed. The temperature of the strong anomaly corresponds to the previously described[6] phase transition at 298 K from the PDN phase **I** (mesophase) to low-temperature phase **II**.

Changes in selected regions of FTIR spectra on cooling are depicted in Figs 2 and 3. The most remarkable changes in the spectra can be observed at temperatures in the vicinity of recorded DSC anomalies.

The first changes concerning intensities and width of particular bands are clearly seen on cooling the sample from 300 to 270 K. The intensities of the bands at 1619, 948, 933 and 397 cm^{-1} are decreasing while those at 1164 and 718 cm^{-1} are increasing. Other changes can be seen on the low-frequency side of the $\nu_3(NO_3^-)$ band and $\omega(CH_2)$ band at 1272 cm^{-1} (decrease). The splitting of combination $\nu_1 + \nu_4(NO_3^-)$ band at ca. 1750 cm^{-1} is also apparent.

Other principal changes in the character of the spectra are observed below 250 K. The most remarkable are the changes concerning the strong complex band in the 1500–1250 cm^{-1} region. Finally, two branches of the $\nu_3(NO_3^-)$ band and several manifestations of $\omega(CH_2)$ vibrations can be clearly distinguished. Another example is splitting of the medium intense band of external vibrations at 162 cm^{-1} to the weak doublet at 175 and 153 cm^{-1}.

If the spectroscopic results are correlated with DSC recordings, it is apparent that the phase transition from phase **I** (mesophase with disordered ions) to phase **II** is associated with minimal changes in overall symmetry of piperidinium and nitrate ions. The only indication of some ordering of ni-

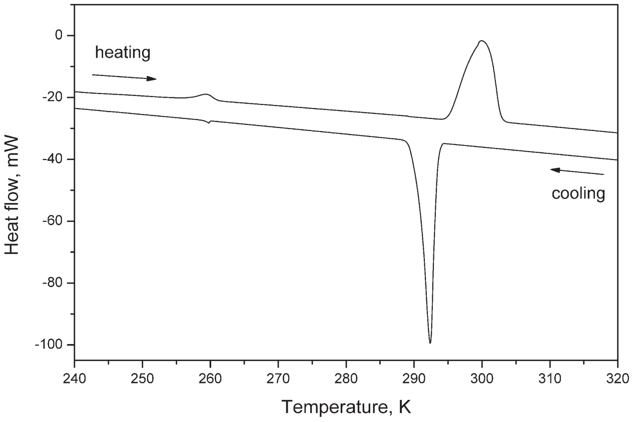

FIG. 4
DSC curves of piperidinium nitrate

trate anions is the changes in the ν_3 region and splitting of the $\nu_1 + \nu_4$ band. Further cooling of the sample below the temperature of 250 K leads to dramatic changes in the spectra. These changes indicate a low-temperature phase transition, which is based on further ordering of nitrates and piperidinium ions associated with lowering of their symmetry (splitting of ν_3 and $\nu_1 + \nu_4$ (NO_3^-) bands, presence of $\nu_1(NO_3^-)$ band in IR spectrum, resolving of $\omega(CH_2)$ bands and splitting of bands of skeletal vibrations). The discussed structural changes are associated with the rearrangement in the hydrogen-bonding scheme in phase **III**. The formation of stronger hydrogen bonds manifests itself in shifts of the high-frequency branch of $\nu(NH_2^+)$ vibrations (–120 cm^{-1}) and the band of $\delta(NH_2^+)$ vibrations (+14 cm^{-1}).

CONCLUSIONS

The results of DSC and FTIR study of piperidinium nitrate indicate the existence of two phase transitions at 295 and 265 K. The first transition (phase **I** → phase **II**) is associated with only minimal changes in the symmetry of ions forming PDN crystals. The second transition (phase **II** → phase **III**) is associated with symmetry lowering as a result of further ion ordering, especially of nitrate anions, and the rearrangement of hydrogen bonds.

This work was financially supported by the Grant Agency of the Charles University in Prague (grant No. 337/2005/B-Ch).

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