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Dedicated to Prof. Dr. H. J. Seifert on the occasion of his 60^{th} birthday

LOW-TEMPERATURE DTA- AND IR-STUDIES ON BARIUM NITROPRUSSIDE TRIHYDRATE, $Ba[Fe(CN)_5NO]\cdot 3H_2O$

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The results of a DTA study between room temperature and 90 K on barium nitroprusside trihydrate, (BaNP), $Ba[Fe(CN)_5NO]\cdot 3H_2O$, complemented by temperature-scanning IR transmission spectroscopy are reported.

Recently, the existence of a phase transition has been reported in Ref. 1 for BaNP, and several studies have been conducted towards the understanding of its crystal structures [2–6]. In this work careful DTA and IR measurements have been carried out to determine the existence and nature of phase transitions in the range 90 K up to room temperature. Interestingly enough, BaNP shows a rich DTA behaviour, as well as $Sr[Fe(CN)_5NO]\cdot 4H_2O$ (SrNP), while the DTA curve of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ is smooth and shows no inflexion points [7, 8]. The transition temperatures and the relative enthalpies associated are reported.

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The vibration bands (IR) as a function of temperature reported for the first time. The results reported in this work have been previously used in the work done by means of ^{14}N Nuclear Quadrupole Resonance ($^{14}N-NQR$) [9, 10].

Also interest in BaNP has been renewed, in particular it is the second of the nitroprusside salts where a long-living electronic metastable state of the anion was produced by laser irradiation at low temperature [1]. It has been demonstrated [1, 11] that for different nitroprussides the relaxation temperature of the metastable electronic states depends on the cation, and therefore on the crystal structure. One of the aims of the present work is to study the low temperature behaviour in order to understand the decay temperatures.

Experimental

Preparation of samples

BaNP was obtained in the usual way, by reaction between $Ag_2[Fe(CN)_5NO]$ (prepared from SrNP and $AgNO_3$ in water) suspended in a slightly-less-than-stoichiometric aqueous $BaCl_2$ solution. The absence of the chloride ion in the solution was taken as the indication of the completeness of reaction. BaNP was crystallized by concentrating the filtered solution in a rotatory vacuum evaporator at room temperature. Infrared powder spectra were run of mulls (in Nujol) between CsI plates. Big single crystals were obtained, for DTA measurements, by the hanging seed method, by spontaneous evaporation of solvent at room temperature from saturated aqueous solutions [12].

DTA measurements

DTA measurements were performed in a home-made apparatus [13], able to detect up to 0.1% C_p anomalies at heating rates between 1 and 5 deg/h, which ensures quasi-static thermodynamic conditions. The core of the instrument is a thick-walled (1 cm thickness) aluminium cylindrical vessel 10.5×17.5 cm, filled with high-density polystyrene, which contains the sample and the reference. As samples, big single crystals up to $2\times1\times0.8$ cm^3 size were used. The reference was a 4.51 g aluminium cylinder.

A thin hole was drilled in the sample up to approximately its centre and filled with APIEZON T grease, in order to ensure good thermal contact with the measuring thermocouple which was inserted in it. Temperature calibration of the DTA apparatus was performed with melting ice and boiling nitrogen. DTA collected consisted of the sample temperature (T_s), the temperature difference between sample and reference (ΔT), and the time (t) at which T_s and ΔT are required.

Runs were performed by cooling the measuring unit with boiling nitrogen and letting it to warm up spontaneously. The lack of a liquid helium facility puts the lower limit of the apparatus at about 80 K. However, the measurements were performed from 90 K upwards. The heating rate between 90 and 240 K was about 3.6 deg/h.

Infrared spectra

IR spectra were obtained with a Perkin–Elmer 580 B spectrophotometer and ancillary IRDS. Cooling was performed with an APD Displex cryogenerator. The lowest temperature attainable was about 20 K but results reported here will be limited also to the same temperature interval as above. Spectra were run at about 10 K intervals when the temperature was far from the transition points an at 3 K intervals around them. Each temperature was kept fixed (within ±2 deg) at least during half an hour. Measurements were made both during cooling and heating. Temperature calibration was performed also with melting ice and boiling nitrogen. Wavenumber calibration was controlled with atmospheric water and CO_2 bands, as well as with polystyrene and SrNP (CN–stretching) bands [14].

Results and discussion

DTA

Figure 1 shows results of a DTA run performed with a single crystal weighing 3.63 g. Three peaks in the ΔT *vs.* T_s curve are clearly seen, at 118.0, 130.2 and 233.4 K (mean values of seven runs) and they were reproducible within ±0.6 deg for different runs and two different samples (taken from different batches). The thermal transition associated with peaks do not seem to be of first order (see below, however) and the relative enthalpies are approximately as follows: $\Delta H_{118.0} : \Delta H_{130.2} : \Delta H_{233.4} = 1:1.4:4.3$ (as calculated from the areas under the peaks). The peak temperatures compare very favourably with values found by $^{14}N-NQR$ (118, 131, 233 K [9, 10]).

Neutron diffraction detected only two transitions at 112 and 130 K [4], and comparative X-ray diffraction results obtained at room temperature and at 150 K were also unable to reveal the high-temperature transition [6]. It is to be noted that in the DSC study of the thermal decay of excited electronic states of the anion in BaNP no structural transition was found between 106 K and room temperature [11], perhaps due to a sensitivity problem (samples were seemingly not more than 20 mg) and to the relatively high heating rate.

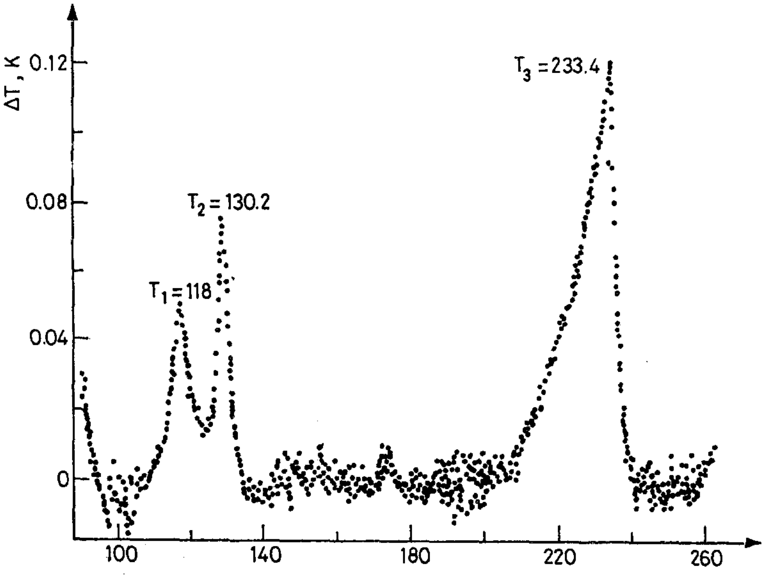

Fig. 1 DTA run of BaNP. The three peaks corresponding to the phase transitions are clearly seen

Again the peaks found by DTA seem to be due to second order transitions because in no case sample temperature stabilization, however short in time, was observed during the transition as expected from the isothermal evolution or absorption of latent heat associated to a first order transition. However, the $^{14}N-NQR$ behaviour of BaNP at 131 K was explained as if the transition, although weak, were of first order. Moreover, the transition at 118 K has a doubtful NQR behaviour which can be interpreted either as pseudo-second order or very weakly first order [9, 10]. Neutron diffractrograms show the reversible appearance and disappearance of reflections forbidden at room temperature, at 112 and 130 K, pointing to structural phase transitions [4]. $^{14}N-NQR$ results indicate a lowering of symmetry of the anion (m to 1) at 233 K and the increase of the number of anions in the asymmetric unit from one to at least two at 131 K, and to an even greater number at 118 K [10]. These changes as well as an anomaly in the relative intensities of the $^{14}N-NQR$ lines and the appearance of weak additional commensurate reflections in the low temperature X-ray and neutron diffraction diagrams have been associated with the peculiar behaviour of the two water molecules [4, 6, 10]. On the contrary, the water molecules in SrNP are all crystallographically equivalent and behave in a normal way [15–17].

The room-temperature crystal structure of BaNP has been refined under the non-centrosymmetric $Pca2_1(C^5_{2v}$, N°29) [2] and the centrosymmetric $Pbcm(D^{11}_{2h}$, N°57) [3, 4, 6], both orthorhombic space groups ($Z=4$). In the latter case two alternatives have been proposed for the location of two of the water molecules which show a peculiar structure behaviour; in one case [3] an ordered model with waters in the m and $\bar{1}$ position has been proposed, while the other involves a split-atom model [4, 6]. The third water molecule has, in both cases m(irror) symmetry. When lowering the temperature below 233 K the abnormal water molecules which at room temperature are perhaps jumping between symmetrically equivalent general positions seem to freeze inducing an NQR-observable asymmetry of the anions. Moreover, a long range ordering of the two abnormal water molecules seems to develop and there appears a pseudo-orthorhombic superstructure, of lower symmetry than the Pbcm subcell, with one of the (super)cell constants doubled with respect to it [6]. At even lower temperatures, the number of formulas in the asymmetric unit of the cell seems to become greater than one [10].

Infrared spectra

IR results seem to confirm the soft character of the phase transitions because changes in the spectra were smooth, as shown by Fig. 2, which reproduces powder spectra obtained at 264, 236, 225, 166, 136, 126 and 107 K. As the spectrum at 87 K looks the same as the spectrum at 107 K it is not included in Fig. 2. Spectra at 20 K of a single crystal (001) can be seen in [1]. Powder spectra are in certain sense superior to single-crystal plate spectra because the plates could not be thinned enough, due to practical limitations, to make them sufficiently transparent in the regions of the strongest absorbances. Table 1 includes wavenumbers and assignments of bands found in the spectra at 264, 166 and 107 K. When cooling the samples, NIR shifts expected from the contraction of the lattice, as well as FIR and also NIR shifts due to hydrogen-bonding [4], the narrowing and changes in the intensities of bands, the definition of shoulders and the appearance of new bands and shoulders are observed. As stated above, changes observed in the spectra seem to be smooth, not abrupt, and take place both in the anion and water vibrational regions.

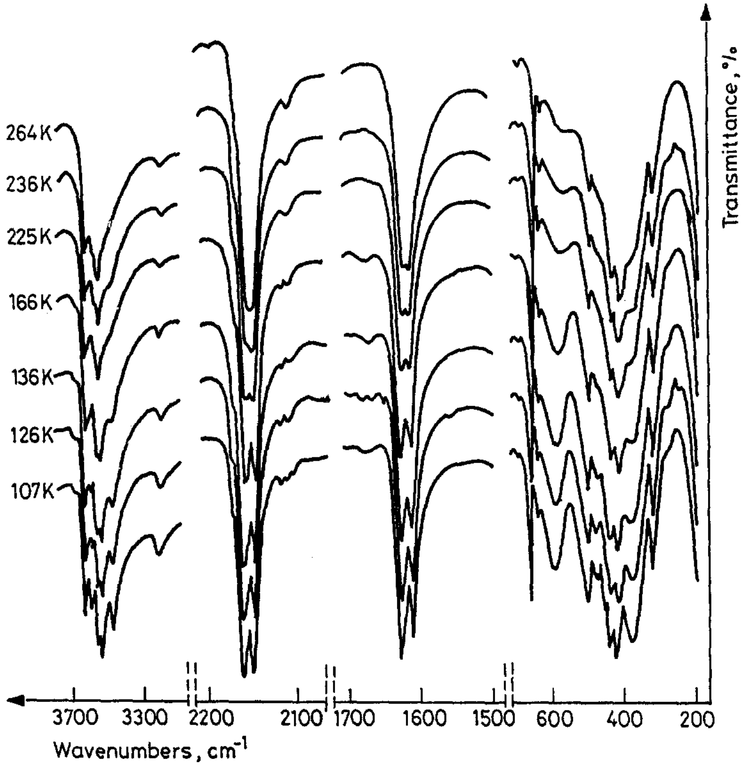

Fig. 2 IR spectra of BaNP at various temperatures. Important changes are to be noted

The most conspicuous facts which occur in the spectra when lowering the temperature are perhaps the following: at about the first transition temperature (233.4 K) the shoulders at 2154 and 1621 cm^{-1} turn into peaks which become more intense than the original. Below 225 K the shoulder at 3509 cm^{-1} turns also into a peak which when lowering further the temperature shifts to 3472 cm^{-1} at 107 K (below the transition temperatures 118.0 and 130.2 K) and stays there. A shoulder at 3604 cm^{-1} appears at 166 K and soon turns into a peak, and the band at 3556 cm^{-1} splits into the 3560 and 3512 cm^{-1} peaks. Below 166 K the shoulder at 3576 cm^{-1} disappears.

Table 1 Infrared spectra at different temperatures (wavenumbers in cm^{-1})

264 K		166 K		107 K		Assignement
3914		3912		3911		?
3871		3873		3876		2ν(NO)
		3672	(sh)	3675		?
3630		3631		3634		ν(H_2O)
				3618	(sh)	
		3604	(sh)	3595		
3576	(sh)	3576	(sh)			
3556		3560		3562		
		3542		3532		
3509	(sh)	3484		3472		
				3432	(sh)	?
		3221		3225		2δ(H_2O)
3211		3214		3212		
2167	(sh)	2170		2171		ν(CN)eq.
2154	(sh)	2158		2159		ν(CN)ax.
2150		2148		2149		ν(CN)eq.
		2117		2117		
2111		2108		2111		ν(^{13}NO)
		2104	(sh)	2106		
1965		1967		1968		ν(NO)
1939		1941		1941		
1910	(sh)	1913		1914		ν(^{15}NO)
1621	(sh)	1627		1629		δ(H_2O)
1616		1614		1613		
664		665		666		δ(FeNO)
649		650		650		ν(FeN)
571		594		599		L(H_2O)
				520	(sh)	?
503		505		506		δ(FeCN) ?
496	(sh)	472		480		L(H_2O)
		456	(sh)	459		δ(FeCN), ν(FeC)
443		445		446		
438	(sh)	437		438		
422		423		425		
				419	(sh)	
414	(sh)	415	(sh)	414	(sh)	
387	(sh)	385		381		L(H_2O)
325		325		325		δ(FeCN), ν(FeC)
				282	(sh)	

In the low-wavenumber region, most of the changes are surely due to librational motions of the water molecules but the splitting at 445 and 437 cm^{-1} (166 K) and the peak at 459 cm^{-1} (107 K) could be traced back to the anion.

The anion bands are in the regions around 2150 cm^{-1} (CN stretchings), 1960 cm^{-1} (NO stretching, not shown in Fig. 2 because not appreciable changes occur in the region), 660 cm^{-1} (FeNO deformation and FeN stretching) and 430 and 300 cm^{-1} (FeCN bendings and FeC stretchings) [12].

The most dramatic change in the anion spectrum is obviously the splitting observed in the CN stretching region, where the room temperature band splits into two bands at 2159 and 2149 cm^{-1} which are possibly due to A' and A'' modes originated in the equatorial $E(C_{4v})$ mode under C_s site-symmetry [5, 12].

Water stretching bands appear in the region around 3550 cm^{-1}. the deformation bands at about 1620 cm^{-1} and librational bands, below 66 cm^{-1} [5, 12]. Splittings observed in these regions confirm the existence of more than one crystallographic type of water molecules in the structure. Detailed discussions on the vibrational behaviour of BaNP at room temperature and below will appear in [5] and [18], respectively. Several questions still remain open, and more work is needed to answer them.

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Zusammenfassung — Ergebnisse einer DTA-Untersuchung von Bariumnitroprussidtrihydrat $Ba[Fe(CN)_5NO]3H_2O$ (BaNP) im Temperaturintervall Zimmertemperatur bis 90 K, ergänzt durch Temperatur-Scanning IR Transmissionsspektroskopie werden beschrieben.