The results of a DTA study between room temperature and 90 K on barium nitroprusside trihydrate, (BaNP), Ba[Fe(CN)$_5$NO]·3H$_2$O, 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)$_5$NO]·4H$_2$O (SrNP), while the DTA curve of Na$_2$[Fe(CN)$_5$NO]·2H$_2$O is smooth and shows no inflexion points [7, 8]. The transition temperatures and the relative enthalpies associated are reported.
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)$_5$NO] (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 $2\times0.8$ 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.