Reaction of barium thiocyanate with trans-1,2-bis(4-pyridyl)ethylene (bpe) in acetonitrile/water using different molar ratios always lead to the formation of a new barium coordination polymer of composition \[
\{[[\text{Ba}(\text{NCS})(\text{H}_2\text{O})_5]\text{]}_2\text{(bpe)}\}\text{(NCS)}_2\text{(bpe)}_3\text{(H}_2\text{O})_2
\] (1). During the preparation of single crystals of compound 1, three additional new compounds were obtained (2–4), of which one crystallizes in two different polymorphic modifications (4I and 4II). In compound 1 the Ba cations are coordinated by six water molecules, two N-bonding thiocyanato anions and one N atom of a bpe ligand within an irregular polyhedron. Two Ba cations are linked by two water molecules and two \(\mu\)-1,1-N-bridging thiocyanato anions into centrosymmetric dimers that are further connected by the bpe ligands into chains. The coordination topology in the crystal structure of compound 2 is very similar to that in 1 in that two coordinating water molecules are exchanged by two terminal bpe ligands. As in 1, Ba dimers are observed that are connected by the bpe ligands into chains. In \([\text{Ba}(\text{NCS})_2\text{]}_2\text{(bpe)}_3\) (3) the barium cations are linked by two \(\mu\)-1,3-bridging anions and one side-on-bridging thiocyanato anion into chains that are further linked by the bpe ligands into layers. In the first polymorphic modification of composition \([\text{Ba}(\text{NCS})_2\text{(bpe)(H}_2\text{O}(\text{CH}_3\text{CN})\text{)]CH}_3\text{CN}\) (4I) each Ba cation is coordinated by one terminal N-bonding and two \(\mu\)-1,1,3(N,N',S)-bridging thiocyanato anions, two bridging water molecules, one acetonitrile molecule and one bpe ligand within an irregular polyhedron. The Ba cations are connected into chains that are further linked via O-H⋯N hydrogen bonding. The crystal structure of the second form 4II is very similar to that of form 4I, and significant differences are found predominantly in the packing of the complexes. Investigations using simultaneous differential thermoanalysis and thermogravimetry on compound 1 have shown that this compound decomposes in three steps with the formation of compound 3 in the second TG step.

**Key words:** Coordination Chemistry, Barium(II) Thiocyanates, Crystal Structures, Thermal Properties