

High-Pressure Polymorphism of 4,4-Bipyridine Hydrobromide

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Abstract : 4,4-Bipyridine is an important compound often used in chemical practice and more recently frequently applied for designing new metal organic framework (MoFs). Here we present a systematic high-pressure study of its hydrobromide salt. 4,4-Bipyridine hydrobromide monohydrate, 44biPyHBrH₂O, at ambient-pressure is orthorhombic, space group P212121 (phase a). Its hydrostatic compression shows that it is stable to 1.32 GPa at least. However, the recrystallization above 0.55 GPa reveals a new hidden b-phase (monoclinic, P21/c). Moreover, when the 44biPyHBrH₂O is heated to high temperature the chemical reactions of this compound in methanol solution can be observed. High-pressure experiments were performed using a Merrill-Bassett diamond-anvil cell (DAC), modified by mounting the anvils directly on the steel supports, and X-ray diffraction measurements were carried out on a KUMA and Excalibur diffractometer equipped with an EOS CCD detector. At elevated pressure, the crystal of 44biPyHBrH₂O exhibits several striking and unexpected features. No signs of instability of phase a were detected to 1.32 GPa, while phase b becomes stable at above 0.55 GPa, as evidenced by its recrystallizations. Phases a and b of 44biPyHBrH₂O are partly isostructural: their unit-cell dimensions and the arrangement of ions and water molecules are similar. In phase b the HOH-Br⁻ chains double the frequency of their zigzag motifs, compared to phase a, and the 44biPyH⁺ cations change their conformation. Like in all monosalts of 44biPy determined so far, in phase a the pyridine rings are twisted by about 30 degrees about bond C4-C4 and in phase b they assume energy-unfavorable planar conformation. Another unusual feature of 44biPyHBrH₂O is that all unit-cell parameters become longer on the transition from phase a to phase b. Thus the volume drop on the transition to high-pressure phase b totally depends on the shear strain of the lattice. Higher temperature triggers chemical reactions of 44biPyHBrH₂O with methanol. When the saturated methanol solution compound precipitated at 0.1 GPa and temperature of 423 K was required to dissolve all the sample, the subsequent slow recrystallization at isochoric conditions resulted in disalt 4,4-bipyridinium dibromide. For the 44biPyHBrH₂O sample sealed in the DAC at 0.35 GPa, then dissolved at isochoric conditions at 473 K and recrystallized by slow controlled cooling, a reaction of N,N-dimethylation took place. It is characteristic that in both high-pressure reactions of 44biPyHBrH₂O the unsolvated disalt products were formed and that free base 44biPy and H₂O remained in the solution. The observed reactions indicate that high pressure destabilized ambient-pressure salts and favors new products. Further studies on pressure-induced reactions are carried out in order to better understand the structural preferences induced by pressure.

Keywords : conformation, high-pressure, negative area compressibility, polymorphism

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